SYNTHESIS, CHARACTERISATION AND APPLICATION OF ORGANIC SURFACTANTS MODIFIED CLAYS FOR WATER PURIFICATION

By

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KEYWORDS

Intercalation, phenols, partition, adsorption, surfactant modified clay, molecular mechanical calculation, isotherm, $p$-chlorophenol, $p$-nitrophenol, application, montmorillonite, organoclays, high resolution thermogravimetric analysis, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Bisphenol A, imazaquin, atrazine, hexadecyltrimethylammonium bromide, cationic surfactant, tetradecyltrimethylammonium bromide, dodecyltrimethylammonium bromide, didodecyldimethylammonium bromide, X-ray photoelectron spectroscopy
ABSTRACT

Natural clay minerals are used as adsorbents for the removal of environmental contaminants due to their structural properties such as high cation exchange capacity, high surface area and high adsorption/absorption. However, because of their hydrophilic nature, their utility for the removal of toxic organic contaminants is limited. To improve their efficiency, the exchangeable cations (Na\(^+\) or Ca\(^{2+}\)) are replaced with quaternary ammonium cations (QACs) through ion exchange. This results in the development of hydrophobic organoclays that are suitable for the removal of organic contaminants.

This research project aims to synthesise organoclays using montmorillonite (MMT) with different types of QACs, describe the structural and thermal properties of the organoclays, and quantify and compare the adsorption efficiencies of the organoclays, which are presented in the form of eight journal articles.

Organoclays were successfully synthesised by intercalating different types of long chain cationic surfactants, including dodecyltrimethylammonium bromide (DDTMA), hexadecyltrimethylammonium bromide (HDTMA), tetradecyltrimethylammonium bromide (TDTMA) and didodecyl dimethylammonium bromide (DDDMA) into montmorillonite at different degrees of organic cation saturation.

Preliminary investigations were carried out to determine the changes in the basal spacing in the interlayer space of the MMT by X-ray diffraction (XRD). The structural configurations of the loaded surfactants and the thermal stability of the organoclays were analysed using thermogravimetric analysis (TG). Through infrared spectroscopy and X-ray photoelectron spectroscopy (XPS), the chemical composition of MMT was identified and the C-C bond and CH stretching region was found to be sensitive to the structural changes in organoclays. The described structural configurations of the surfactants were qualitatively confirmed using the molecular mechanical calculation (MM calculation). These results have indicated that the loading of surfactants into MMT caused a transformation of the surface property of the clays from hydrophilic to hydrophobic. In particular, at the higher surfactant loadings, the organoclays intercalated with the larger organic cations (e.g. HDTMA.
and DDDMA) tended to have a larger basal spacings, suggesting the potential benefits of the transformation for the removal of organic contaminants.

The fully characterised organoclays were investigated as potential adsorbents for the removal of phenolic compounds (e.g. $p$-nitrophenol and $p$-chlorophenol), bisphenol A, BPA, imazaquin and atrazine from aqueous solutions. It was found that organoclays intercalated with organic surfactants (e.g. HDTMA and DDDMA) were suitable to adsorb phenolic compounds, BPA and imazaquin. In particular, at the higher saturations of organic cations the organoclays intercalated with the large organic cations had a strong tendency to adsorb more organic pollutants. However, the organoclays were not efficient for the removal of atrazine. Further investigation was conducted under different experimental conditions (e.g. agitation time, pH, temperature and different concentrations of pollutants) in order to optimise the adsorption of the organic pollutants and to identify the mechanisms in the adsorption system. Different adsorption behaviours of the organoclays towards the organic pollutants were demonstrated.

Finally, this thesis demonstrated the adsorption of various types of organic pollutants by montmorillonite modified organoclays, and promoted the potential application of organoclays as adsorbents in industry and the environment. Overall, the adsorption processes were simple and efficient, and the high removal rate of the emerging endocrine disrupting pollutant, BPA has brought the merits of the organoclays for water purification system in industry and the environment to the forefront of clay utilisation. As an outcome, this investigation offers a more optimistic evaluation of organoclays for the removal of recalcitrant organic molecules compared with other adsorbent materials, and the current findings point to promising applications for environmental remediation. Furthermore, the use of the MM calculation provides a stepping stone for demonstrating the configurations of organic molecules within the interlayer space of MMT and the observed structural and thermal properties of MMT and organoclays. This thesis has enhanced the understanding of organoclays and assisted in their assessment for more beneficial use in a wide range of industrial applications.
PUBLICATION AND CONFERENCE PRESENTATIONS

List of Papers produced from this investigation


Conferences papers:


Papers not presented in this thesis:


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<th>Description</th>
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<tbody>
<tr>
<td>BET</td>
<td>Brunauer, Emmett, and Teller</td>
</tr>
<tr>
<td>BPA</td>
<td>Bisphenol A</td>
</tr>
<tr>
<td>DDDMA</td>
<td>Didodecyldimethylammonium bromide</td>
</tr>
<tr>
<td>DDTMA</td>
<td>Dodecyltrimethylammonium bromide</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared spectroscopy</td>
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<td>HDTMA</td>
<td>Hexadecyltrimethylammonium bromide</td>
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<tr>
<td>MM calculation</td>
<td>Molecular mechanical modelling calculation</td>
</tr>
<tr>
<td>MMT</td>
<td>Montmorillonite</td>
</tr>
<tr>
<td>TDTMA</td>
<td>Tetradecyltrimethylammonium bromide</td>
</tr>
<tr>
<td>PCP</td>
<td>$p$-chlorophenol</td>
</tr>
<tr>
<td>PNP</td>
<td>$p$-nitrophenol</td>
</tr>
<tr>
<td>PPCPs</td>
<td>Pharmaceutical and Personal Care Products</td>
</tr>
<tr>
<td>QACs</td>
<td>Quaternary ammonium cations</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimetric analysis</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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STATEMENT OF ORIGINAL AUTHORSHIP

The work contained in this thesis has not been previously submitted to meet requirements for an award at this or any other higher education institution. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made.

Signature: ____________________________

Date: 14/0ct/2013
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CHAPTER 1
INTRODUCTION
1.1 Assessment of scientific problems investigated

Water is essential to food security, health, industrial output, and the quality of our environment. One of the problems that is associated with water quality is the presence of water contaminants derived by human activity: from inorganic/organic compounds (e.g. heavy metals, polycyclic aromatic hydrocarbons (PAHs), herbicides and pesticides) and distillates to emerging pollutants (e.g. endocrine disrupters and nitrosamines) in many freshwaters [1]. Progressively, public health and environmental concerns have driven greater research efforts aimed at the development of water treatment techniques, including membrane filtration, electrochemical technique, photo-catalysis, and adsorption [2, 3]. Of the techniques that have been proposed, adsorption methods are widely applicable techniques that are fast and require lower cost [3]. In particular, there is a need finding effective, inexpensive, and efficient materials for the adsorption processes.

To address this issue, the use of clay minerals have been suggested for the removal of water contaminants due to their properties: (i) clays have a high cation exchange capacity and high surface areas, which confer strong adsorption/absorption properties, and (ii) clays are naturally abundant in Australia, in particular South Queensland has large deposits of bentonite clays. Their efficiencies have been expanded remarkably by replacing exchangeable inorganic cations with organic cations to yield hydrophobic organoclays for the removal of organic contaminants. Recently, organoclays have been used to remove oil and other organic contaminants from water [4-12]. However, they are far less studied and comprehensively explored as adsorbents for emerging pollutants such as hormones and pharmaceuticals, which are the main obstacles to overcome for recycled water to be accepted by the community.

To elucidate the potential of organoclays for their environmental remediation purpose, their structural and thermal properties need to be fully understood. It is known that organoclays can be prepared with different types of cationic surfactants, and that previous studies [13, 14] have investigated the configuration of surfactant molecules within $d_{(001)}$ spacing of clays and structural stabilities using X-ray diffraction (XRD) and thermogravimetric analysis (TG). In the current study, infrared spectroscopy and X-ray photoelectron spectroscopy (XPS) provided in-depth information about the molecular structural information and the binding energy in organoclays. The employment of molecular mechanical calculation (MM
calculation) visually supports the changes in the structural configuration of surfactant molecules within the interlayer space of clays. Once the structural characteristics of the organoclays were known, they were tested as potential adsorbents to remove selected organic contaminants (e.g. phenolic compounds, herbicides and pesticides, and pharmaceutical and personal care products- PPCPs).

1.2 Research objectives of the study
The overarching objective of the study was to synthesise organoclays with different types of surfactant molecules for environmental remediation. The prepared organoclays were fully characterised using various techniques and tested under laboratory scale for their adsorption capacity to remove organic contaminants and emerging water pollutants from water.

The specific aims of this thesis are to:

- Investigate the effect of surfactant loadings on the structural configurations of organoclays.
- Investigate the effect of different types of surfactants (mono- and di-cationic surfactants) to provide information that enable a comparison of the structural properties of organoclays.
- Examine the thermal stabilities of organoclays.
- Simulate the conformational changes of surfactants in the interlayer space.
- Test and compare the efficiencies of organoclays for the removal of organic water contaminants.
- Investigate the effect of kinetics, thermodynamics and different concentrations of pollutants that are associated with the adsorption capacities of the organoclays for the removal of organic pollutants
- Explain the mechanisms involved in the adsorption of the organic water pollutants using the organoclays.
1.3 Research methodology

To fulfil the research objectives in this study, an outline of the research plan is described in the following flow chart (Figure 1-1). The flow chart also presents the structure of the thesis systematically, including the research outputs.

In the thesis, a literature review that focused on three elements: (i) the potential of unmodified clays and organoclays as adsorbents, (ii) numerous instrumental techniques that are employed to characterise the materials, (iii) the application of materials for the removal of various industrial pollutants from aqueous solutions was undertaken. This scientific review was published as a full peer-reviewed article in the *Journal of Colloid and Interface Science* [15].

Drawing from the comprehensive literature review, the thesis was designed to describe the physical and chemical properties of the organoclays and evaluate their potentials for the removal of organic pollutants, including emerging pollutants from aqueous solutions. A series of research investigations were focused on organic environmental contaminants derived from agricultural and industrial activities commonly found in aqueous solutions.

Throughout the PhD, a series of peer-reviewed international journal articles [16-20] and manuscripts have been published or submitted.

1.4 Characteristics of montmorillonite

A clay mineral is a layered silicate mineral or a phyllosilicate and one of the smectite group clay minerals, montmorillonite, has been used in this PhD work. Montmorillonite is produced by volcanic and hydrothermal activity and composed of hydrous aluminium silicates. Its chemical structure is $A_{0.3}(Al_{1.3}Mg_{0.7})[Si_4]O_{10}(OH)_2\times H_2O$, where A is an exchangeable cation (e.g. $K^+$, $Na^+$, or $0.5Ca^{2+}$ etc). Depending on the mineral origin, the charge exchange capacity (CEC) of the montmorillonite ranged from 0.9 to 1.2 mequiv/g [21]. Standard Swy-2 montmorillonite is mainly composed of 75 % smectites and small amount of impurities such as quartz, feldspar, kaolinite, plagioclase, orthoclase and opal [22]. The properties of montmorillonite including chemical mineral composition and
specific surface area (SSA) and cation exchange capacity (CEC) are summarised in Table 1.1.

**Table 1.1 Mineral properties of Swy-2-montmorillonite**

| SiO₂ | Al₂O₃ | TiO₂ | Fe₂O₃ | FeO | MnO | MgO | CaO | Na₂O | K₂O | P₂O₅ | CEC (meq/100g) | SSA (m²/g) |
|------|-------|------|-------|-----|-----|-----|-----|-----|-----|-----|------|---------------|-----------|
| 62.9 | 19.6  | 0.09 | 3.35  | 0.32| 0.006 | 3.05 | 1.68 | 1.53 | 0.53 | 0.049 | 76.4 | 31.82         |

The unique feature of montmorillonite structure is that water and other certain organic substances can enter between the unit layers, causing swelling and expansion in the direction to the basal plane [23]. Through inorganic exchange reactions, montmorillonites react with and tend to absorb some organic substances. The crystal lattice of montmorillonite consists of 1 nm thin layers, with a central alumina octahedral sheet between external silicate tetrahedral sheets. It is known that montmorillonite has two kinds of electric charges: a variable charge and a structural negative charge, resulting from proton adsorption/desorption reactions on the surface hydroxyl groups and isomorphous substitution within the clay structure, respectively [24]. The negative potential from the isomorphous substitution is responsible for the electrical, sorptive and coagulative properties of the particles. Therefore, this negative potential of montmorillonite causes a negative electrophoretic mobility and cation adsorption and cation exchange properties. Montmorillonite is particularly used to slow the progress of water through soil or rocks. It is useful industrially in drilling muds to give the water greater viscosity, and used to produce nanocomposites and to purify and decolour liquids as an adsorbent. It is also widely used in medicine and pharmacology [25].

1.5 Account of scientific progress linking the scientific papers

In developing the methodology, the title of the study is “Synthesis, Characterisation and Application of Organic Surfactants Modified Clays for Water purification”. The details from the investigation were presented as follow:
1.5.1 Review the potential of unmodified and modified clay minerals as adsorbents for the removal of water contaminants (Paper 1)

A review was published that highlighted an upsurge of interest in the removal of industrial pollutants from aqueous solutions. The review showed that enhancing the structural properties of clay minerals using organic cations that cause the conversion of the clay into hydrophobic organoclays increases the potential of these materials as adsorbents. The modification, which is usually accomplished through ion exchange, leads to an increase in the basal spacing of the clays and the creation of new sorption sites. In this regard, organoclays with larger basal spacings will be expected to be efficient adsorbents for the removal of water contaminants (e.g. phenolic compounds, pesticides/herbicides, and anionic contaminants). One of the important key criteria in the synthesis of organoclays was the selection of organic cations that can lead to the formation of different organoclays (either adsorptive clays or organophilic clays), that demonstrate different sorption behaviours in environmental applications.

Recently, the detection of pharmaceutical and personal care products (PPCPs) in water has been of a great public and environmental concern [26]. In practice, the developed organoclays have not completely been explored as potential adsorbents for the removal of emerging pollutants (e.g. hormones and pharmaceutical products) and thus this issue is addressed in this project and is as shown in Paper 7 (submitted for publication) in Chapter 8.

1.5.2 Synthesis of organoclays (Papers 2 – 4)

Following the literature review of the use of organoclays for environmental remediation, it was necessary to determine which clay minerals were to be used in this investigation. It was considered that due to their beneficial properties a clay from the smectite group, montmorillonite (MMT), would be useful for this investigation. Because, MMT has a 2:1 expanding crystal lattice, consisting of two siloxane tetrahedral sheets with a central alumina octahedral sheet and possesses high exchange capacity (CEC), swelling properties, high surface areas and consequential strong adsorption/absorption it was considered to be a good choice for the project [27]. The results obtained from the use of modified MMT are presented in published Papers 2 – 4 (Chapters 3 – 5).
To synthesise the organoclays, it was also necessary to choose suitable organic surfactants to improve the adsorption capacities of the prepared organoclays as effective materials for the removal of recalcitrant organic contaminants. Given that in a number of reports, long-alkyl groups (e.g. DDTMA, TDTMA, HDTMA, DDDMA) have enhanced the adsorption properties of organophilic clays, and are likely to lead to organoclays with large basal spacings, and as such were selected as good candidates to fulfill the objectives of this project. These findings are presented in published Papers 2 – 4 (Chapters 3 – 5) [6, 10, 28].

1.5.3 Characterisation of organoclays (Papers 2 – 6)
A number of publications in the scientific literature have provided essential information on X-ray diffraction (XRD), thermogravimetric analysis (TG), vibrational spectroscopy (Infrared spectroscopy), X-ray photoelectron spectroscopy (XPS), surface analyser and electron microscopy (e.g. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)) to determine the structural and thermal properties of synthesised organoclays. In this project, an additional measurement that was applied was the molecular mechanical calculation (MM calculation) and this technique enabled the visualisation and confirmation of the arrangement of intercalated surfactant molecules in the interlayer space of the clays. The method was beneficial for monitoring and validating the experimental data, presented in numerous publications in the Journal of Colloid and Interface Science and Chapters 6 – 7.

The experimental details and the structural and thermal properties of organoclays intercalated with long chain surfactants (HDTMA, DDTMA, DDDMA and TDTMA) have been described and published in journal articles in Chapters 3 – 7 [16, 18-20].

1.5.4 Potential use of organoclays for the removal of organic contaminants from aqueous solutions (Papers 5 – 8)
Earlier Papers 2 – 6 had determined the characteristic features of organoclays. This investigation tested the adsorption efficiency of organoclays for the removal of various organic pollutants from aqueous solutions. Accordingly, several types of organic water pollutants produced from industrial and agricultural activities were included in the investigations (i) phenolic compounds (p-nitrophenol and p-
chlorophenol), (ii) pharmaceutical and personal care products (bisphenol A), and (iii) herbicides and pesticides (imazaquin and atrazine).

To identify more qualitative information on the mechanisms involved in the adsorption of organic pollutants, the experimental studies were designed and conducted using different experimental conditions, including agitation time, temperature, pH, and different concentrations of pollutants.

The efficiencies of the organoclays for the removal of a wide range of organic pollutants prepared using the different conditions were tested and compared. The summarised results of the work have been published and/or submitted for consideration for publication [16].

Overall, this thesis is presented in the form of eight published or submitted articles, which address the major objectives of the project and described the state of knowledge on the use of organoclays for the removal of recalcitrant organic water pollutants. In addition, the synthesis and characterisation of various types of organoclays prepared by the modification of montmorillonite by cationic organic surfactants, and their respective adsorption properties have been assessed for the removal of common and emerging environmental pollutants.

1.6 References


Chapter 1: Introduction

Chapter 2: Literature review (Paper 1)

Synthesis and Characterisation of Organoclays

Chapter 3: Synthesis and characterisation of organoclays intercalated with HDTMA (Paper 2)

Chapter 4: Synthesis and characterisation of organoclays intercalated with DDTMA and DDDMA (Paper 3)

Chapter 5: Synthesis and characterisation of organoclays intercalated with TDTMA (Paper 4)

Application of Organoclays for the removal of organic pollutants

Phenolic compounds

Chapter 6: Adsorption of PCP and PNP by organoclays intercalated with HDTMA (Paper 5)

Chapter 7: Adsorption of PCP and PNP by organoclays intercalated with DDTMA and DDDMA (Paper 6)

Pharmaceutical and Personal Care Products

Chapter 8: Adsorption of BPA by organoclays intercalated with HDTMA, DDTMA and DDDMA (Paper 7)

Herbicides and Pesticides

Chapter 9: Adsorption of imazaquin and atrazine by organoclays intercalated with HDTMA, DDTMA and DDDMA (Paper 8)

Chapter 10: Conclusions and Recommendations for future work

Figure 1.1 Flow diagram indicating research progress and associated publications
CHAPTER 2
LITERATURE REVIEW

This review paper was originally published:

PREFACE

Water is widely contaminated by recalcitrant organic chemicals such as pesticides, herbicides and hormones. One of the inexpensive methods used to purify water and remove the various chemicals that contaminate is through the adsorption process. One suite of materials commonly used for this adsorption is based on modified clays or organoclays. Hence, this paper was written to review the extensive literature available that describes the adsorption of organics on organoclays.

The literature review has reported that organoclays have been applied in many different environmental applications. Recent papers have supported the effectiveness of organoclays for the uptakes of organic contaminants such as aromatic organic compounds, phenolic compounds, pesticides and herbicides and other pollutants in contaminated water. This paper also summarises a number of characterisation techniques utilised for the characterisation of organoclays such as X-ray diffraction (XRD), thermogravimetric analysis (TG), vibrational spectroscopy, surface area analyser, and electron microscopy.
STATEMENT OF CONTRIBUTION OF CO-AUTHORS

The authors listed below have certified* that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and
5. they agree to the use of the publication in the student’s thesis and its publication on the QUT ePrints database consistent with any limitations set by publisher requirements.

In the case of this chapter:


<table>
<thead>
<tr>
<th>Contributor</th>
<th>Statement of contribution*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yuri Park (candidate)</td>
<td>Wrote the manuscript</td>
</tr>
<tr>
<td>Godwin A. Ayoko (Principal Supervisor)</td>
<td>Revised and edited the manuscript</td>
</tr>
<tr>
<td>Ray L. Frost* (Associate Supervisor)</td>
<td>Revised and edited the manuscript</td>
</tr>
</tbody>
</table>

Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

[Signature]

Name    Signature    Date

15
2.1 Introduction

The production of purified water is essential to living organisms and the human races’ health, food security, and well-being [1]. In the modern society, a primary environmental issue is the quality of surface water, sediments, ground water and drinking water. Many of the world’s waterways and sources are contaminated with a range of chemicals from point and non-point sources. Consequently, purification of contaminated water is critical and there has been an upsurge of interest in a variety of materials that can be used to remove water contaminants [2].

Of the materials that are available for the removal of water contaminants, activated carbon is a well-known material for water purification all over the world because of its high surface area, porous structure, and special surface reactivity [3, 4]. The porous nature, inertness and thermal stability of activated carbon are favourable properties of adsorption [5-7]. Although the adsorbent material has a great capacity for adsorption of water pollutants, its widespread use is limited due to its high cost [8]. Therefore, effective and economic adsorbents have been investigated, and particularly, clay minerals [9-11] have drawn attention as suitable materials for oil remediation and removal of toxic chemicals from water.

The naturally abundant clay minerals are widely used in a range of applications such as polymer nano composites, catalysts, photochemical reaction agents, and adsorbents [2]. Among other applications, clays have extensively been used as adsorbents for water purification due to their high cation exchange (CEC), swelling properties, and high surface areas [12-14]. Generally, clay minerals are hydrous aluminosilicate with very fine particle size.

The most used clays as adsorbents are montmorillonite/smectite groups which refer to non-metallic clays composed of hydrate sodium aluminium silica with a formula of (Ca,Na,H)(Al, Mg, Fe, Zn)2(Si,Al)4O10(OH)2·nH2O, and kaolinite group clays with the general formula of Al2Si2O5(OH)4. The montmorillonite/smectite is a clay that has 2:1 expanding crystal lattice and its basic structure is a layer consisting of two inward pointing tetrahedral sheets with a central alumina octahedral sheet. Due to the isomorphous substitution, various types of smectite are available including dioctahedral minerals (e.g. montmorillonite, beidellite, nontronite, and bentonite), and trioctahedral minerals (e.g. hectorite, saponite, and sauconite). In addition, the
isomorphous substitution causes a net negative charge on the clay surface by the replacement of Mg$^{2+}$ or Zn$^{2+}$ for Al$^{3+}$ in the octahedral layer, and Al$^{3+}$ for Si$^{4+}$ in the tetrahedral sheets [15]. The layers are continuous in the length and width directions, but the weak bonds between layers allow water and other molecules to intercalate into the interlamellar space of clay which leads to an expansion of the minerals. The 2:1 layered silicate montmorillonite swells when it contacts water and shrinks when dried.

The kaolinite group includes the dioctahedral minerals (e.g. kaolinite, dickite, nacrite, and halloysite), and the trioctahedral minerals (e.g. antigorite, chamosite, chrysotile, and cronstedite) is composed of one octahedral sheet condensed with one tetrahedral sheet and it is called 1:1 layer silicate. The octahedral site is occupied by mainly Al$^{3+}$ in the dioctahedral, whereas these sites are filled by Mg$^{2+}$ and Fe$^{2+}$ in trioctahedral minerals (see Table 2.1).

**Table 2.1 Characteristics of clay minerals [16]**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Molecular formula</th>
<th>CEC$^a$ (cmol/kg)</th>
<th>OC$^b$ (%)</th>
<th>OM$^c$ (%)</th>
<th>Surface area (m$^2$/g)</th>
<th>$d_{(001)}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite$^e$</td>
<td>(Na,Ca)$_{0.33}$(Al,Mg)$_2$(Si$<em>4$O$</em>{10}$)</td>
<td>82</td>
<td>0.06</td>
<td>0.10</td>
<td>750</td>
<td>13.38</td>
</tr>
<tr>
<td>Kaolinite$^f$</td>
<td>Al$_2$Si$_2$O$_5$(OH)$_4$</td>
<td>6.1</td>
<td>0.10</td>
<td>0.17</td>
<td>12</td>
<td>7.16</td>
</tr>
<tr>
<td>Illite$^g$</td>
<td>(K,H$_2$O)(Al,Mg,Fe)$_2$(SiAl)$<em>4$O$</em>{10}$[(OH)$_2$,(H$_2$O)]</td>
<td>15</td>
<td>1.74</td>
<td>2.99</td>
<td>57</td>
<td>10.04</td>
</tr>
<tr>
<td>Muscovite$^h$</td>
<td>KAl$_2$(AlSi$_3$O$_10$)(F,OH)$_2$</td>
<td>21</td>
<td>0.10</td>
<td>0.17</td>
<td>105</td>
<td>10.04</td>
</tr>
<tr>
<td>Sepiolite$^i$</td>
<td>Mg$_4$Si$<em>6$O$</em>{15}$(OH)$_2$·6H$_2$O</td>
<td>5.0</td>
<td>0.08</td>
<td>0.13</td>
<td>189</td>
<td>12.16</td>
</tr>
<tr>
<td>Atapulgite$^j$</td>
<td>(Mg,Al)$_2$Si$<em>4$O$</em>{10}$(OH)-4(H$_2$O)</td>
<td>27</td>
<td>0.96</td>
<td>0.79</td>
<td>254</td>
<td>10.64</td>
</tr>
</tbody>
</table>

$^a$ Cation exchange capacity (CEC). $^b$ Carbon contents (OC). $^c$ Organic matter contents (OM).

$^d$ Montmorillonite impurities

$^e$ Tidinit montmorillonite (Morocco).

$^f$ Cuenca kaolinite (Spain).

$^g$ Fithian illite (Illinois).

$^h$ Penausende muscovite (Spain).

$^i$ Vallecas sepiolite (Spain).

$^j$ Bercimuel Atapulgite (Spain).
There has been increasing interest in utilizing natural clays such as montmorillonite, kaolinite, illite, and bentonite for the removal of toxic metals and organic contaminants from aqueous solutions [17-19]. Even though their natural porous structure offers a great potential for the retention of pollutants, many studies [20, 21] reported that naturally occurring clays are ineffective for the adsorption of anionic contaminants, and hydrophobic or non-polar organic pollutants. This is due to the hydrophilic characteristics of their surfaces and charges.

Recently, many studies [22-28] have investigated their increasing adsorption capacity for organic contaminants. They reported that the adsorption of various organic compounds by clay minerals have been greatly improved by replacing the natural inorganic interlayer cations with certain organic cations such as quaternary ammonium cations (QACs), which may be represented as \([((\text{CH}_3)_3\text{NR})^+]\), or \([((\text{CH}_3)_2\text{NR}_2)^+]\) where \(R\) is a relatively short hydrocarbon substituent group. The aluminosilicate sheets of common clay minerals possess a net negative electrical charge compensated for by inorganic exchange cations (e.g. \(\text{Na}^+\) and \(\text{Ca}^{2+}\)), which are strongly hydrated in the presence of water. Surface properties of natural clays can be modified by simply ion exchange with organic cations. By introducing cationic surfactant molecules into the interlamellar space through ion exchange, the properties of clay minerals are enhanced to those of organoclays [29, 30]. The intercalation of a cationic surfactant between the clay layers changes the surface properties from highly hydrophilic to increasingly hydrophobic. In addition, modification of the swelling clay with a cationic surfactant results in an increase in the basal spacing of the layer and exposure of new sorption sites of clays (see Table 2.2).

**Table 2.2 List of examples for organic cationic surfactants on the exchange complex of clay minerals**

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Didodecyldimethylammonium</td>
<td>DODMA⁺</td>
<td>(\text{CH}_3(\text{CH}<em>2)</em>{10}\text{CH}_3)</td>
</tr>
<tr>
<td>Octadecyltrimethylammonium</td>
<td>ODTMA⁺</td>
<td>(\text{CH}_3(\text{CH}<em>2)</em>{17}\text{CH}_3)</td>
</tr>
<tr>
<td>Name</td>
<td>Abbreviation</td>
<td>Structure</td>
</tr>
<tr>
<td>------------------------------------</td>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Hexadecyltrimethylammonium</td>
<td>HDTMA⁺</td>
<td><img src="image" alt="HDTMA Structure" /></td>
</tr>
<tr>
<td>Benzyltrimethylammonium</td>
<td>BTMA⁺</td>
<td><img src="image" alt="BTMA Structure" /></td>
</tr>
<tr>
<td>Benzyltriethylammonium</td>
<td>BTEA⁺</td>
<td><img src="image" alt="BTEA Structure" /></td>
</tr>
<tr>
<td>Trimethylphenylammonium</td>
<td>TMPA⁺</td>
<td><img src="image" alt="TMPA Structure" /></td>
</tr>
<tr>
<td>Tetramethylammonium</td>
<td>TMA⁺</td>
<td><img src="image" alt="TMA Structure" /></td>
</tr>
<tr>
<td>Benzyldimethyltetradecylammonium</td>
<td>BDTMA⁺</td>
<td><img src="image" alt="BDTMA Structure" /></td>
</tr>
<tr>
<td>Dodecyltrimethylammonium</td>
<td>DTMA⁺</td>
<td><img src="image" alt="DTMA Structure" /></td>
</tr>
<tr>
<td>tetraethylammonium</td>
<td>TEA⁺</td>
<td><img src="image" alt="TEA Structure" /></td>
</tr>
</tbody>
</table>
From several studies [31, 32], organoclays are classified into two different groups including adsorptive clays and organophilic clays by the structure of QACs and the mechanism of adsorption behaviour.

The first group called adsorptive clays are synthesised with QACs contains short-chain alkyl groups and/or a benzyl group, such as benzyltriethylammonium (BTEA) or tetramethylammonium (TMA)/trimethylphenylammonium (TMPA). Sorption on this type of organoclay is characterised by Langmuir-type isotherms, which are commonly associated with specific sorption sites. On the other hand, if the QACs contain a long-chain alkyl group, such as hexadecyltrimethylammonium (HDTMA) and didodecyldimethylammonium (DODMA) clays, the group of organoclays is called an organophilic clay. The sorption of this group is characterised by linear isotherms over a wide range of solute concentrations. The different sorption behaviour of the two organoclays (adsorptive clays and organophilic clays) is further described in their environmental applications. The modified clay derived from long chain alkylammonium ions creates an organic partition medium through the conglomereration of the flexible alkyl chains, whereas the clay from small quaternary ammonium ions does not form partition phases. Instead surface adsorption sites for non ionic solute uptake exist as discrete entities on the clay layers because of the small alkyl-chain ions [31, 33]

The size of alkyl chain length and the charge density of clay layers are responsible for the arrangement of intercalated organic cations in the organoclays [34]. In the classic model, the organic cations only form monolayers in the adsorptive clays intercalated with short chain alkyl ammonium ions. In contrast, bilayers, pseudo-trimolecular arrangement or paraffin complexes may be found in the organophilic clays intercalated with long surfactant cations (see Figure 2.1).

The arrangement of surfactant alkyl chains can also be incorporated with the conformational changes of C-C bonds (kicks) [35]. It can be assumed that three layer structures of kinked alkyl chains (pseudo-trimolecular layers), are formed by kicks, where some chain ends are shifted above one another. Using FT-IR, $^{13}$C-NMR and DSC techniques, the qualitative information of interlayer structure, chain conformation and dynamics of organoclays intercalated with alkyl ammonium cations has been obtained [36-38]. As the new computational modelling calculation
has been developed, more detailed description of chain conformations in the interlayer space can be yielded [39, 40].

As the highly charged clay minerals intercalate with alkylammonium ions, more paraffin-type structures can be formed [35]. Figure 2.2 describes the relationship between the arrangement of alkylammonium ions in interlayer space with alkyl chain length and layer charge of clay.

Figure 2.1 The classic model of arrangement of alkylammonium ions (adapted from the work by Lagaly et al. [34])

Figure 2.2 Effect of layer charge and chain length on the arrangement of alkylammonium ions [35]
The organoclays are extensively investigated for a wide variety of environmental applications because of their unique sorption capabilities. In particular, hydrophobic organoclays become effective adsorbents to remove organic pollutants. There are many investigations on the adsorption and the application of organoclays for effluents treatment, remediation of ground water and encapsulation of solid waste. Moreover, the organoclays are applied to remove several water pollutants such as organic compounds, pesticides and herbicides, anionic contaminants, heavy metals, and pharmaceutical products in water. The main goal of this review is to provide a summary of information concerning the use of organoclays as adsorbents, particularly, for the removal of aromatic organic compounds, phenolic compounds, pesticides and herbicides and other pollutants in contaminated water.

2.2 Synthesis and characterisation

2.2.1 Synthesis of organoclays

As mentioned above, clay minerals consist of small crystalline particles with silica oxygen tetrahedral sheets and aluminium or magnesium octahedral sheets where an aluminium or magnesium ion is octahedrally coordinated to six oxygens or hydroxyls. The octahedral sheet is located between two Si tetrahedral sheets. Organoclays or organo-montmorillonites are clays that have been modified with organic surfactants with single and dual cationic surfactants, anionic-cationic surfactants and non-ionic surfactants. The structure and properties of the resultant organoclays are affected by both the type of surfactant and clay minerals. The chemical composition of clays varies by the magnitude of the cation exchange capacity (CEC) arising from isomorphous substitution, which involves the substitution of Al\(^{3+}\) for Si\(^{4+}\) in the tetrahedral layer and Mg\(^{2+}\) or Zn\(^{2+}\) for Al\(^{3+}\) in the octahedral layer and results in a net negative surface charge on the clay layer. This charge imbalance is offset by exchangeable cations typically Na\(^{+}\) and Ca\(^{2+}\) at the clay surface [41]. From the ion exchange reaction, the interlayer spacing between the single sheets is broadened. This enables the adsorption of organic cation chains, and changes the surface properties of each single sheet from hydrophilic to hydrophobic or organophilic.

The interlayer cation density or packing density of the alkylammonium ions of the clay minerals and the chain length of the organic ion are important factors to determine the arrangement of organic molecules between the layers as illustrated in
Figure 2.3. The formation of monolayers, bilayers and pseudotrimolecular layers of alkylammonium ions in the interlayer spaces of montmorillonite was characterised by the basal spacings.

![Image of basal spacings](image)

Figure 2.3 Variation of basal spacings of alkylammonium montmorillonites as a function of chain length (Reproduced with the kind permission of the Mineralogical Society of Great Britain & Ireland from a paper by Lagaly et al. [42])

### 2.2.2 Characterisation of organoclays

After the synthesis of organoclays by intercalating organic surfactants into the layers of the clays through ion exchange reactions, various modern characterisation tools, which include determination of properties such as structure, expansion capacity, layer charge, pore size, crystalline size, charge distribution and pore distribution, are available for both naturally occurring clays and synthesised organoclays.

The structural properties of the organoclays are highly dependent on the structure and molecular environment of the organic surfactants. The essential instrumentations used to determine the characteristics of clays and their modified organic derivatives are: X-ray diffraction (XRD), Thermogravimetric analysis (TG), Fourier Transform Infrared spectroscopy (FT-IR), Brinier, and electron microscopy such as Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). Brunauer-Emmett-Teller (BET) is also used as a specific surface area measurement of organoclays.
X-ray diffraction (XRD) is one of the most important techniques to determine the structural geometry, texture and also identify impurities in layer silicates which are present in clays. Generally, XRD can offer basal spacing information on the organoclays used. The results of XRD can also provide information on molecular structure configuration of the surfactant intercalated, including lateral monolayer, lateral bilayer, pseudo-trilayer, paraffin monolayer, and paraffin bilayer. The change of basal spacings often indicates that organic cation surfactants are intercalated within the interlayer of organoclays and d(001) spacings of ion-exchanged natural clays with the same intercalants always compare favourably [43]. However, more evidence of organic uptake is essential for the supposition obtained from the change of basal spacings as XRD does not provide detailed information about the local conformation and phase state of the intercalated surfactants [44]. Hence, this is done by TG and FT-IR.

The thermal stability of the organoclays can be determined by the use of TG [45-47]. Typical TG curves run in an oxygen atmosphere, to optimize organic degradation and the weight loss of a sample, can be observed as a function of temperature (dynamic heating) or time (isothermal heating). A peak at the low temperature (between 60 – 70 °C) is caused by the loss of water from the surface and interlayers, while the high temperature peak (between 700 – 750 °C) is due to the dehydroxylation of the clay layers. It is often convenient to resolve thermal reactions by plotting the derivative of the TG curve. The differential TG (DTG) is a preferred method to determine inflection point of mass loss. The differential scanning calorimetry (DSC) can be employed to describe the interlayer structure of organoclays by measuring the amount of energy adsorbed or released at constant temperature [48]. However, differential thermal analysis (DTA) is the primary tool for the investigation of the thermal properties and reactions of minerals and organoclays [49]. It is based on the heat differences associated with both the physical and chemical changes of a sample compared to a thermally inert reference material. Using DTA, one can measure all reactions and processes that involve a change in energy during heating and/or cooling of a sample including dehydration, dehydroxylation, structural decomposition and transformation [50].

The presence of organic molecules in the clay layers can be determined by using infrared spectroscopy followed by TG. IR technique is an essential method to probe
the molecular orientation of the intercalated surfactant within the organoclays. Generally, FT-IR has been applied for identification of clay structure and is completed after XRD and TG. Detailed information about the interlayer structure and phase state of surfactants in the clay interlayer is critical for understanding the effectiveness of the surface treatment and role in the formation of organoclay [51-53]. Besides, Raman spectroscopy is a powerful technique used to probe the microstructural environment of organic compounds within organoclays at various temperatures.

By introducing BET gas adsorption theory [54], the surface area of organoclays can be determined in the presence of N$_2$. When N$_2$ gas penetrated onto the organoclays, the surface area, pore volume and size distribution of the organoclays are measured and in the process, neutral N$_2$ will attach by Van der Waal’s force to form a single layer, and then multilayer adsorption will take place. However, only external surface can be attached with N$_2$ gas as the gas can move through the interlayer vacancies.

The electron microscopy analysis such as TEM and SEM are employed to make a direct observation of macrostructural features on organoclays. TEM demonstrates the packing density of organoclays within the clay interlayer space and SEM micrographs show surface morphology of clay and organoclay samples [55].

Besides, the UV-Vis spectroscopy is applicable to investigate the association between organic cation molecules on the clay surface. In the study of Budjak and Iyi [56], the aggregation behaviour with organic dyes and montmorillonites is monitored by using UV-Vis spectroscopy. When organic dyes are intercalated with clay minerals, the visible range spectrum is shifted, which is ascribed to the chemical changes in the chromophores. By introducing UV-Vis spectroscopy, more useful information can be obtained on the characteristics of organoclay particles.

2.3 Application of organoclays as adsorbents

2.3.1 Adsorption of aromatic organic compounds

About 35 million tonnes of aromatic compounds have been released from petroleum products such as gasoline, jet fuel, or diesel fuel in the environment and these pollutants have contributed to the pollution of groundwater contaminants [57]. Hence, presence of organic compounds as contaminants in the environment is of great
concern. Among a range of other adsorbents, organoclays have been employed in environmental cleanup applications.

From the study of Sheng et al. [58], clay minerals have excellent capabilities for cations and polar molecules that arise from the large specific surface area, and negative charges caused by isomorphic substitution [15]. In addition, polar organics such as alcohols, amines, and ketones were adsorbed into the external clay surface, interlayer space and probably on clay particle edges by electrostatic attraction and ion exchange reactions. However, clay minerals still have a greater tendency to adsorb inorganic cations in wastes than organic constituents due to the large size of organics and hydrophilic nature of clays. Hence, the clay minerals are generally ineffective sorbents for hydrophobic or non-polar organic pollutants [21]. Since the hydrophilicity of clay minerals decreased through the addition of QACs, the resulting organoclays can adsorb non-ionic organic compounds (NOCs) from aquatic solutions [29, 33, 59-61] and have been suggested for wastewater treatments.

The hydrophobic organoclays with high uptake capacity of organics have actually been employed to remove aromatic wastes from water and the effectiveness of organoclays for the remediation of organic contaminants was seven times more powerful than using the activated carbon [62]. Boyd and Jaynes [59, 63] investigated the adsorption behaviour of organic compounds in water by using several organoclays formed by replacing the inorganic exchange cations with different organic cations. When organoclays with large organic cations such as hexadecyltrimethylammonium (HDTMA) or benzyldimethyldodecylammonium (BDTMA) was used, the adsorption of benzene and alkylbenzenes increased. On the other hand, the adsorption of aromatic hydrocarbons was increased when organoclays with small organic cations such as tetramethylammonium (TMA) or trimethylphenylammonium (TMPA). Hence, they concluded that the adsorption behaviour of organoclays is influenced by the molecular structure of the exchanged organic cations and the length of alkyl chain.

They also investigated the nature of siloxane surface in smectite by measuring the adsorption of aromatic hydrocarbons from water. They observed that the adsorption of aromatic hydrocarbons from water yielded a Langmuir-type isotherm and concluded that the surface area occupied by each adsorbed molecule increases as the
planar area of the molecule increases. The study of Sheng et al. [64] showed that aqueous phase NOCs such as benzene, nitrobenzene, chlorobenzene, trichloroethylene, and carbon tetrachloride were significantly removed by using layer silicate clays modified with HDTMA. In the comparison of long and short chain organoclays, the long alkyl chain organoclays are more effective adsorbents for NOCs than the short alkyl chain organoclays [32]. Depending on the type of QACs used for modification based on the previous study, the clays resulting from the cation exchange reactions can be classified into two categories: (i) adsorptive organoclays produced from relatively small QACs and (ii) organophilic clays, which are produced from monovalent, long-chain alkyl QACs.

Recent studies have extensively investigated the adsorptive characteristics of organoclays for NOCs in terms of magnitude and mechanisms for understanding, predicting, and maximising their sorptive capabilities and for designing new families of organoclays. Numerous researchers [31, 60, 65-67] reported that the adsorption of NOCs to organophilic clays derived from long-alkyl chains such as HDTMA or BDTDA is characterised by relatively low solute uptake, isotherm linearity, partition behaviour, correspondence between organic carbon normalised sorption coefficients ($K_{oc}$) and the octanol water partition coefficients ($K_{ow}$), and inverse dependence on water solubility. In contrast, sorption of NOCs to adsorptive clays modified from short alkyl chains such as TMA or TMPA is characterised by relatively strong solute uptake, isotherm nonlinearity, shape selectivity, surface adsorption behaviour, and progressively lower uptake of larger aromatic molecules.

The ability of organoclays sorbents to selectively remove lower molecular weight hydrophobic organics from water in the presence of larger, more hydrophilic organics was investigated by Dentel et al. [66]. 1,2,4-trichlorobenzene (TCB), as an example of low molecular weight NOCs, was removed from water in the presence of tannic acid and the adsorption of organoclays to remediate TCB from aqueous solution was caused by a portioning mechanism and adsorption capability increased in the order: TMA<HDTMA<HDBDMA<DDDMA, which is compatible with the order of the organic carbon contents of these clays. In addition, TCB was adsorbed from water by the modified clays with no significant competition from tannic acid, which does not affect the basal spacings of the organoclays. Furthermore, Sheng et al. [60] reported that the sorptive characteristics of organoclays for NOCs were
controlled by multiple mechanisms including salvation of the cationic ammonium centres, the alkyl chains of HDTMA and the mineral surfaces and solute partitioning.

A comparison was made of the characteristics and mechanism of polar and non polar organic solute sorption from water to Cetyltrimethylammonium bromide (CTMA)-bentonite by Zhu et al. [67], and similar sorption properties of organoclays were produced. Nonpolar organic compounds such as benzene, toluene, ethylbenzene sorption to Cetyltrimethylammonium bromide (CTMA)-bentonite from water was caused primarily by partitioning as indicated by relatively low solute uptake and linear isotherms whereas the sorption of polar organic compounds including phenol and $p$-nitrophenol to CTMA-bentonite was caused more by adsorption or other interaction than by partition. In addition, the removal efficiencies and sorption capacities of organic compounds from water by organobentonite were enhanced as the concentrations of QACs increased.

Koh and Dixon [26] demonstrated that the sorption of NOCs such as phenol, benzene, and toluene are dependent on the Ca/Mg cation exchange capacity (CEC) of each mineral in the order: Na-montmorillonite > zeolite > sericite. Among the surfactant organic cations with various molecular weights, the aliphatic tail on the BDTDA ion apparently contributed to the multiple interlayer in BDTDA in contrast to benzyltrimethylammonium (BTMA)’s reluctance to sorb a second interlayer. Hence, BDTDA-montmorillonite has the most potential for application as a sorbent of three NOCs. In addition, its sorption effectiveness for benzene and toluene continued to increase with each increase in the surfactant to montmorillonite ratio.

In order to find the optimal mass of cationic surfactant on the bentonite, various ratios of HDTMA to bentonite were prepared by Lee and Park [68]. Chlorobenzene and lead was selected as representative contaminants and either chlorobenzene or lead existed as a single contaminant, adsorption of chlorobenzene increased with increasing ratios of HDTMA to bentonite, while the lead sorption decreased with increase ratios of HDTMA to bentonite. The opposite sorption of chlorobenzene and lead can be assumed that the lead sorption was much more affected by the initial concentration than by the added mass of HDTMA. On the other hand, the removal rate of chlorobenzene was significantly increased by coverage of cationic surfactant, and it is suggested that the use of 100 %-organobentonite is the most effective to
remove both organic contaminants and heavy metal (less than 0.5 mg/L) as the removal rate of chlorobenzene by 100 % organobentonite was about four times higher than that of chlorobenzene by untreated bentonite.

The amount and size of the surfactants added on the clay was also found by Lee et al. [69] to be responsible for the sorption of non-ionic hydrophobic organic compounds (HOCs). The sorption of HOCs such as naphthalene and phenanthrene by HDTMA-modified smectite linearly increased with an amount of HDTMA added to the clay. However, the sorption of HOCs reduced when TMA- and DTMA-smectite applied and the sorption capability partially decreased at specific surfactant loading levels. Hence, they assumed that not only the amount and size of the surfactants but also the interlayer structure formed at each surfactant loading level play important roles on the uptake of HOCs.

The linear adsorption phenomena in aqueous non-ionic organic solute were characterized by Su et al. [70]. The adsorption isotherm of some low molecular weight non polar ionic solutes (1,2,3-trichlorobenzene, lindane, phenanthrene, and pyrene) and polar non-ionic solutes (1,3-dinitrobenzene and 2,4-dinitrotoluene) from single and binary solute solutions were established. In addition, the influence of temperature, ionic strength, and pH on adsorption was also determined. The results indicated that linear adsorption exhibits low exothermic heats with no adsorptive competition. In addition, the adsorption of non-polar solutes is not influenced on ionic strength or pH while the uptake of polar solutes was influenced significantly.

Oyanedel-Craver et al. [71] showed that the simultaneous and significant sorption of benzene and metals occurred for both organoclays (HDTMA-bentonite and BTEA-bentonite). The decrease sorption capacity of both BTEA and HDTMA clays indicated that there is competition between metals and organic compounds during sorption onto both organoclays. However, generally, great competition effects were observed on BTEA-bentonite in comparison with HDTMA-bentonite. Therefore, the mechanism and magnitude of competitive sorption of non-polar compounds and metals were influenced by QACs, the solubility and physical structure of the NOCs and concentration of the mix of compounds in solution.

Some recent papers showed that modified organoclays with HDTMA can be used to adsorb not only aqueous phases of NOCs but also volatile organic compounds
(VOCs) such as chlorobenzene and trichloroethylene [72, 73]. This offers a potential application of organobentonites for the removal of organic vapours from flue gases and for assessing the efficiency of vapour removal.

2.3.2 Adsorption of phenolic compounds (phenols and its derivatives)

The presence of phenols in water causes an unpleasant taste and odour, and this type of organic pollutant is considered as a priority pollutant. According to the Environmental Protection Agency, USA, priority pollutants are identified as hazardous chemicals to human health and the environment even at low concentrations [74]. Phenols are detected in groundwater or wastewater as a result of industrial activities such as herbicides, pesticides, papers, paint, resin, coke manufactures, and dying industries. Most phenols tend to be present in water because of its relatively high water solubility [75]. Hence, potential exposure of this toxic chemical to human life and the environment is an important issue, and therefore, adsorption techniques to remove this toxic and hazardous contaminant have been developed. Activated carbon is the most popular sorbent for the removal of phenols from wastewaters and ground waters [5, 8, 76]. However, there are some drawbacks, such as regeneration of activated carbons, intra-particles resistance in adsorption process in practice, and high cost of manufacture. Recently, Rytwo and Gonen [77] reported the sorbent properties of organoclay for organic dyes and environmental pollutants. One of the significant advantages for organoclays over activated carbons is the fast adsorbing kinetics, which is an important factor in water purification. Therefore, the inexpensive and fast sorbent organoclays are considered as an alternative material for activated carbon and thus adsorption of phenolic compounds by organoclays has been studied (see Table 2.3).

Table 2.3 Characteristics of compounds

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Water solubility at 25°C (g/kg H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>C₆H₆O</td>
<td>91.7</td>
</tr>
<tr>
<td>Aniline</td>
<td>C₆H₇N</td>
<td>35.0</td>
</tr>
<tr>
<td>2-Chlorophenol</td>
<td>C₆H₅ClO</td>
<td>23.2</td>
</tr>
<tr>
<td>3-Chlorophenol</td>
<td>C₆H₅ClO</td>
<td>22.0</td>
</tr>
<tr>
<td>4-Chlorophenol</td>
<td>C₆H₅ClO</td>
<td>26.2</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>C₆H₅Cl</td>
<td>0.49</td>
</tr>
</tbody>
</table>

*Note: CRC Handbook of Chemistry and Physics, 91st ed. CRC Press, Boca Raton, Fl.*
The potential of natural bentonite for the adsorption of phenols from aqueous solutions has been studied by Benat et al. [18]. The study revealed that the adsorption capacity of bentonite was limited to the adsorption of phenols from water in the treatment of wastewaters. They investigated the main factors that influence the adsorption capability of phenols. From their study, the adsorption capacity was increased at low pH. It was also found that the type of solvent in which phenol was dissolved affected the uptake of phenol-bentonite. Among the prepared solvents (cyclohexane, water, and methanol), the affinity of phenol for bentonite in the presence of cyclohexane was greater than that in water. On the other hand, the adsorption of phenol was lowest in the methanol. The sorption equilibrium data in the different type of solvent was well represented by the Langmuir and Freundlich isotherms. The removal of phenol from aqueous solutions was observed without surface modification.

Recently, many studies have used organoclays synthesised with QACs such as HDTMA clays, TMA clays, and TMPA clays, to improve the adsorption capability of phenol and its chlorinated congeners. The synthesis was introduced by Mortland et al. [78] and the sorption capacity of phenols and its chlorinated congeners were improved when the modified montmorillonite with HDTMA or TMPA were applied. They found that the utilisation of modified clays with TMPA maximised the adsorption capacity of phenol while phenol contaminants in the water were not sorbed by HDTMA-clay even though they have similar structure and interlayer spacings of the corresponding organoclays. Furthermore, the adsorption of phenols and chlorinated phenols was independent of the water solubility of the solute. The adsorption characteristics of phenol and its chlorinated congeners with organobentonite were further examined by Lin and Cheng [79]. The organobentonite was prepared by modifying natural bentonite with several quaternary ammonium salts including tetramethylammonium bromide (TMA), hexadecyltrimethylammonium bromide (HDTMA), benzyltriethylammonium bromide (BTEA), tetraethylammonium bromide (TEA) and cetylpyridinium bromide (CP). They observed that BTEA-bentonite performed the best, with an efficiency of over 80 % for phenol or m-chlorophenol adsorption while the efficiency of TMA and TEA-bentonites was less than 40 %. The empirical Freundlich isotherm was found to describe well the equilibrium adsorption data.
In addition, numerous authors [21, 30, 80, 81] reported that the adsorption of organic contaminants from water by organoclays were influenced by the size, structure, and arrangement interlamellar QACs. Lawrence et al. [80] investigated the adsorption of phenol and 2-, 3-, and 4- chlorophenol from water by organoclays with QACs including TMA and TMPA. Adsorption capacity results indicated that TMPA-smectite was a better adsorbent than TMA-smectite, which did not measurably adsorb any of the phenol compounds. They assumed that the high degree of hydration of the TMA cation in the smectite caused a smaller interlayer pore size for the TMA-smectite than in TMPA-smectite, and the hydration renders the organoclays unable to accommodate space for the phenol in its interlayer region. It was also observed from their study that TMPA-smectite was very selective sorption within the group of chlorinated phenols; phenol and 4-chlorophenol were effectively adsorbed, whereas there was no adsorption of 2- and 3- chlorophenols. Hence, Lawrence et al. [80] concluded that the size and shape were highly responsible for the selectivity adsorption by TMPA-clay for phenol and monochlorinated phenols.

The adsorption behaviour of surfactant-modified bentonite with phenol and chlorinated phenols were also examined by Rawajfih and Nsour [81]. The organoclays synthesised by replacing adsorbed Na+ with HDTMA, which is a long alkyl chain QACs were prepared. The sorption capacity of phenols were increased with chlorine addition (phenol<p-chlorophenol<2,4-dichlorophenol) and the amount of addition of chlorine added was proportional to their hydrophobicities. In other words, the adsorption behaviour was affected by the properties of phenols.

In addition, the studies of Shen et al. [21] indicated that the effects of charge characteristics including charge density and exchanged cation of clay were important on the phenol sorption of organoclays. Shen utilised the organo-smectites synthesised by BTMA as a short alkyl chain and HDTMA as a long alkyl chain. Both BTMA and HDTMA adsorption may be influenced by the effect of charge density on the smectite and results appear to be related to size and molecular arrangement of the exchanged organic cations in the clay. Its study suggested that to form a more effective organic phase for phenol sorption, high charge smectite should be applied for the preparation of organoclays intercalated with a long alkyl chain of organic cations (e.g. HDTMA). However, a short alkyl chain of organic cations (e.g. BTMA) was used for low charge smectites. A similar finding was reported by Zhou et al. [30].
Some researchers were interested in the organoclays intercalated with transition metal complexes to see the adsorption behaviour of phenols [82-85]. Ogawa et al. [83] studied the interaction of photoactive species such as tris(2,2’-bispyridine)ruthenium(II) (abbreviated as [Ru-(bpy)3]2+) intercalated in layered solids, especially in smectites. On the other hand, Okada et al. [84] investigated the adsorption of phenol on mono, bis and tris [Ru-(bpy)3]2+-saponite and tris(ethylenediamine)nickel(II)-saponite interaction compounds. They observed that the adsorption of phenol on the tris(ethylenediamine)nickel(II)-saponite was less than that on [Ru-(bpy)3]2+-saponite and they assumed that the interaction between pyridine rings and phenol might be important for the adsorption of phenol. Furthermore, the group of Okada et al. [85] also utilised tris[Ru-(bpy)3]2+-clays as adsorbent for the removal of phenols (phenol, 4-chlorophenol, and 2,4-dichlorophenol). The adsorption isotherms of phenols for tris[Ru-(bpy)3]2+-clays from aqueous solutions followed Langmuir type, which indicates strong adsorbate-adsorbent interactions. The change of the basal spacings of tris[Ru-(bpy)3]2+-clays was not observed and it indicated that the adsorbed phenols existed in the interlayer nanopore creased by the tris[Ru-(bpy)3]2+ in the interlayer space of the tris[Ru-(bpy)3]2+-clays. In addition, they reported that the adsorbed amount of phenols varied when different clay materials with different CEC were applied. Therefore, the layer charge density of clays which correlated with pore size and volume plays an important role in the increase of the adsorption capacity of phenols, especially the low-layer charge density of saponite with [Ru-(bpy)3]2+ provides relatively a large amount of adsorption of phenols. Furthermore, the adsorption behaviour of organoclays modified with transition metal complexes also depended not only on the layer charge density but also the nature of the exchanged complex from the study of Boufatit et al. [82].

In previous studies, the concentration range of the phenol solution was kept narrow and the pH was not adjusted or higher than 7. Recent work [4, 75, 86-91] has investigated the influence of pH, temperature changes, and the concentration of adsorbent on the behaviour of organoclays used for the removal of phenol compounds.

According to the study of Yilmaz et al. [90], the adsorption of phenol on tetradecyltrimethyl bromide (TDTA) and HDTMA – bentonite was conducted at pH
5.5 and 20 °C. Adsorption efficiencies were defined in terms of relative increase in adsorbed amounts, and HDTMA-bentonite was found to be better. However, there is no specific isotherm equation that gives the best fit for the whole range of both isotherms. In addition, the studies of Yapar et al. and Zhou et al. [86, 91] found that increased concentration of surfactant cations (HDTMA), correlated with increased adsorption of p-nitrophenol in montmorillonite clays.

On the other hand, Xu and Zhu [89] examined the structures and characteristics of organoclays for phenol on hexamethonium bromide (HM)-bentonite and TMA-bentonite in aqueous solutions. Adsorption of phenol on 0.3 CEC-HM is higher than that on 0.6 CEC-TEM at low phenol concentrations. However, it is lower at high phenol concentrations. In addition, the adsorption capacity of phenol on HM-bentonite increased with increasing HM loading under 0.4 CEC, but it decreased when HM loading was over 0.4 CEC. From the obtained results, the contribution of siloxane surface and CECs on sorption process of organic contaminants are important roles for the designing of high efficient organoclay adsorbents, and therefore, they concluded that for the removal of low concentration phenol from water, QACs with proper alkyl should be chosen to synthesise high effective organoclay adsorbents, while more siloxane surface may be the primary factor for the removal of high concentration phenol.

In addition, numerous authors [87, 88] further investigated the effects of adsorption for phenol compounds by organoclays, and they suggested that the adsorption of phenol compounds was affected by the concentration, solubility, and log $K_{ow}$ of sorbates, temperature, kinetic reaction time, and steric contour of organics. Langmuir isotherm has found to be a successful application in sorption processes and a pseudo second order mechanism is determined. Smaller particle size of clays which have more surface area, lower pH, higher temperature promotes the adsorption of more phenol molecules. The rate of removal of phenol is observed to increase as the concentration of sorbate increases while the percentage of adsorption of phenol decreases as the concentration increases.

Huang et al. [4] suggested the potential of octadecyltrimethylammonium chloride (ODTMA) modified atapulgite (AT) for phenol adsorption from aqueous solutions. The adsorption study was carried out to evaluate the effect of contact time, shaking
frequency, temperature and the amount of AT. They suggested that ODTMA-AT is useful to use in the treatment of phenol in aqueous solutions and 60.4 % of adsorption rate was achieved at the optimum conditions: 60 mins of shaking time, 2.5 g of AT, 25 °C and shaking frequency of 140 rev/min. A pseudo-second order model was described and the Freundlich isotherm was found to be applicable for the adsorption equilibrium data.

Furthermore, the thermodynamic study of the adsorption process on phenol compounds to clay was introduced by Alkaram et al. [92]. In their study, the adsorption of phenol with adsorbents was controlled by temperature, and at higher temperature, the adsorption capabilities of phenol increases. This indicates that the adsorption of phenol is controlled by an endothermic reaction. A close look at the thermodynamic parameters, indicate that the negative free energy, $\Delta G$, corresponds to the spontaneous physical process during the adsorption of phenol, and especially, the free energy gains higher negative values when the temperature decreases. The mean adsorption enthalpy, $\Delta H$ values are positive, which also indicates an endothermic reaction. Hence, the adsorption of phenol with adsorbents was carried out spontaneously and the process can be controlled by the endothermic reaction.

2.3.3 Adsorption of pesticides and herbicides

Recently, there has been growing an interest in the use of organoclays to prevent and remediate environmental contaminants like pesticides and herbicides as a result of agricultural activities [93-99]. An increasing use of agrochemicals may result in serious potential health and environmental problems associated with the presence and accumulation of pesticides in soil and ground water. The adsorbed chemicals such as acidic herbicides are not readily degradable by soil particles, soluble in water, and move rapidly with the infiltrating water. Thus these chemicals are likely to be found in the surface and ground waters [25]. These highly mobile compounds can be restricted in order to reduce potential surface and ground water contaminants, and one of the suggested materials in the restriction is organoclays which can be added as controlled release formulations in pesticides and herbicides.

According to Boyd and Brixie [100], organoclays have a strong immobilisation effect on non-ionic organic chemicals with low water solubility. Therefore, the organoclays are also proposed to be carriers of controlled-release formulations to
reduce the pesticides/herbicides leaching through soil to the water [101, 102]. The efficiency of ODTMA-organoclays was measured in the immobilisation of organic pesticides in a sandy soil and the result indicated that the mobility of pesticides (linuron, atrazine and metalaxyl in a sandy loam soil) was reduced by the organoclays modified with the cationic surfactant ODTMA. Almost complete immobilisation of linuron, the most hydrophobic pesticide, and a decrease of the less hydrophobic atrazine and metalaxyl were observed.

Acidic herbicides used in agriculture such as bentazone, dicamba, 2,4-D, cyclopyralid, fenuron and picloram are very mobile and highly water-soluble herbicide if they reach high concentration in soil. In the studies of Hermosin and Cartizosa and other authors [103, 104], organoclays as possible carriers in controlled-release formulations for bentazone and dicamba as an example of mobile and persistent acidic herbicides reduced the total leaching losses from 55 % to 90 %, and reduced fenuron up to 78 %. Their finding suggested the potential use of organoclays as barriers for immobilising pesticides and herbicides derived from point sources, thereby preventing the pollution from spreading through the soil and later contaminating ground waters [16, 25, 94, 96, 98].

Some other studies on the application of organoclays as adsorbents have been reported. From previous studies, clay minerals have been shown to be very good adsorbents for cationic and highly polar pesticides, whereas its adsorption capacity for poorly soluble NOCs was usually low. On the other hand, the modified clay minerals obtained by the replacement of natural inorganic exchange cations with organic cations through the ion exchange reaction increased the performance of the adsorption of NOCs including hydrophobic pesticides [96, 102, 105].

Previous studies on the mechanism of adsorption for NOCs, here also shown that organoclays with long-alkyl chain cations are highly effective adsorbents for NOCs. Groisman et al. [32] investigated the efficiency of organoclays with different sizes of alkyl chains in removing organic pollutants from the pesticides mixtures. The sorption by a long-chain ODTMA-organoclay is less affected by competition with accompanying compounds and background materials, while a short-chain TMA-organoclay is very sensitive by competition. Hence, the use of long-chain organoclays is preferred to remove pesticides from industrial wastewater.
Carrizosa and colleagues [25] further investigated the influence of adsorption-desorption of dicamba, selected as a model of very mobile and leachable herbicides. Two smectites (SAz and SWy) were reacted with different amounts of alkylammonium cations such as octadecyl (C18)-, hexadecyltrimethyl (HDT)-, and dioctadecyldimethyl (DOD)- ammonium of 50 % or 100 % of the CEC of the clays. As a result, the adsorption capacity of dicamba on organoclays is increased due to high layer charge, alkylammonium size, and saturation of bulky organic cation close to CEC. The hydrophobic and polar interactions are responsible for the adsorption of dicamba by organoclays, which are needed for the availability of interlayer space between organic cations in the organoclays. On the other hand, the desorption isotherms were reversible except in organoclays with C18 and DOD cations as a result of the stronger polar contribution in the primary alkylammonium and the difficulty for diffusion in the bulky organoclays. Similar adsorption behaviour of the herbicide prometrone by diverse organoclays was observed by Socias-Viciana et al. [106].

Essential characteristics for the adsorption for pesticides and herbicides are high layer charge, quaternary alkylammonium and organic cation saturation below CEC [95, 107, 108]. These characteristics are responsible for the promotion of sorption by organoclays.

In previous studies, the most commonly used organic cations for the improvement of adsorption capacity of clay minerals have been the quaternary ammonium ions containing alkyl or aryl chains without specific functional groups. However, Cuz-Gruzman [96] investigated the ability of organoclays prepared by replacing the organic exchangeable cations with diverse functional groups (L-carnitine, L-cystine dimethyl ester, and thiamine) to control the adsorption efficiency of herbicide simazine. It appeared that the specific interlayer microenvironment provided by the functional groups of each organic cation was an important factor controlling the adsorption efficiency of the modified clays. The adsorption for carnitine, cysteine dimethyl ester in simazine was considerably significant than that of organoclays intercalated with classical alkylammonium cations such as phenyltrimethylammonium or hexadecyltrimethylammonium. Therefore, they suggested that the modification of organoclays with natural organic cations with
appropriate functional groups can be useful in improving the performance of organoclays for the removal of organic pollutants from the environment.

Based on the potential influence of diverse functional groups of organic cations on the clay, the capacity and selectivity of adsorption behaviour of organoclays for pesticides with functional polar groups were investigated [109]. From the observations, they concluded that adsorption capacity and selectivity of organoclays was influenced by the presence of functional groups in the organic cations. It was suggested that chemical characteristics of the organic cation can optimise the adsorbent properties compared to the use of alkylammonium cations, which lack specificity.

In addition, a new type of organoclays called bifunctional organoclays has been introduced by Groisman [110]. This new organoclay is able to adsorb organophosphate pesticides and then catalysts their hydrolysis, which detoxifies the pollutants. Although the mechanistic details of the reaction have not yet been fully investigated, the catalytic effect of the bifunctional organoclays on the hydrolysis of phosphate esters was clearly demonstrated and the catalytic effect was highly related to the proximity induced between the reacting groups by the organoclay structure.

### 2.3.4 Adsorption of other pollutants (anionic contaminants, heavy metals and pharmaceuticals)

Presence of high concentration of landfill leachate such as metal cations, anions, and organic compounds cause a great threat to nearby groundwater [111]. Due to the negative charge of soil particles, adsorption of anionic contaminants such as chromates is limited by the regular clay liners. Chromium is one of the most abundant inorganic groundwater contaminants at hazardous waste sites and the use of inexpensive adsorbent materials have been investigated recently [112-116]. Clay minerals demonstrated high potential for applications as environmental remediation agents to remove chromate from water include smectite, kaolite, illite, palygorskite and sepiolite.

From Li and Bowman’s group [114], the clay minerals modified by cationic surfactant to twice their cation exchange capacities were able to sorb nitrate and chromate significantly. In addition, they conducted studies on modified organo-illite with long hydrophobic groups such as HDTMA. It was found that it was an effective
sorbent for anionic contaminants and has been used to prevent migration of contaminants anions in applications such as landfill liners.

The influences of the adsorption capacity of chromate were investigated by Hong et al. [112]. The rectorite was modified by steary trimethylammonium chloride (STAC) or octadecyltrimethylammonium chloride (ODTMAC) and the adsorption of Cr(VI) was tested as a function of pH, temperature, and initial chromate to rectorite ratio at batch scales. It was concluded that the Cr(VI) adsorption by STAC-modified rectorite is strongly dependent on pH as STAC-rectorite adsorbs chromate effectively in acidic solutions. The adsorption of Cr(VI) was maximised at pH 4 and the enthalpy change of the adsorption is -9.4 kJ/mol, indicating retention of Cr(VI) on STAC-rectorite is via physical adsorption. They assumed that the uptake of negatively charged Cr(VI) ions in the interlayer regions of STAC-modified rectorite is due to electrostatic forces derived from the polarised water molecules and positively charged groups of the STAC cations. Similar results were found by Krishna et al. [117, 118] and they revealed that pH is highly responsible for the adsorption capacity of organoclays modified with HDTMA. It was found that the amount of adsorbed chromate decreased with increasing pH and become negligible above pH 8. Thermodynamic parameter for surfactant sorption on montmorillonite and Cr(VI) sorption was investigated by using modified clay. The specific rate constant of Cr(VI) species on modified montmorillonite was rapid and equilibrium was attained within 30 mins. The process followed the first order kinetics.

The pH influences the concentration of Cu, Pb, and Cd in the effluent [119]. For example, Na-montmorillonites are good adsorbents towards examined metals, and the amount of sorption of metal ions on modified clay has been shown to increase with increasing solution pH [120]. Lothenbach et al. [121] also investigated the effect of pH on the removal of nickel, copper, and zinc using modified montmorillonite. It was observed that Al-montmorillonite were the most effective in the pH range 6 – 8 for nickel and zinc, 4 – 6 for copper, and 7 – 9 for cadmium. Modified clays (coated by aluminium) are more efficient in immobilising heavy metals than untreated montmorillonite at pH above 6.

More recently, pharmaceutical and personal care products (PPCPs) have been discovered in various surface and ground waters [122]. These PPCPs including
antibiotics, endocrine disrupting chemicals (EDCs), and veterinary pharmaceuticals are emerging pollutants and these compounds have been linked to a variety of adverse effects in both humans and wildlife at trace concentrations [123]. Hence, reports of EDCs and PPCPs in water have raised substantial concern among the public and regulatory agencies. However, information on the fate of these compounds during drinking and wastewater treatment is limited. Numerous studies have shown that many of PPCPs and EDCs do not fully degrade during municipal wastewater treatment and highly mobile pharmaceuticals have the potential to leach into the groundwater as well as accumulate in the top layer of soil. Therefore, organoclays have been suggested as absorbents for ground and surface water treatment of toxic organic chemicals including PPCPs.

Among PPCPs, antibiotics or anti-microorganisms are a major class of pharmaceutical of concern because the presence of antibiotics in the environment changes microbial ecology. Furthermore, the presence of antibiotics can cause disturbance in water treatment processes, which are based on bacterial activities. Tetracycline and sulphonamide (sulfa drug) antibiotics are widely used as human and veterinary pharmaceuticals and both groups undergo slow degradation and transformation [124]. The remediation of large molecules of tetracycline and sulphonamide antibiotics in the presence of dissolved organic matter (DOM) is highly complicated. Therefore, the application of montmorillonite modified with benzyldimethylhexadecylammonium (BDMHDA) was introduced. The efficiency for the removal of two antibiotic groups from water was demonstrated and based on the results, it was concluded that BDMHDA micelle-montmorillonite system is very efficient for the removal of both tetracycline and sulphonamide antibiotics from water in the presence of DOM.

In addition, the removal of the nicotine and its pharmaceutical derivatives from aqueous solution was assessed by using bentonite and dodecylammonium-bentonite (DAB) by Akcay et al. [125]. Although the nicotine can be easily removed by bentonite as characteristics of $K_f$ and $n_f$, which refers to characteristic constant parameters of adsorbate/adsorbent systems, the DAB has been found to be a better adsorbent than bentonite for the removal of nicotine and pharmaceutical derivatives from aqueous solution. The positive surface charge can remove small molecules and polarise toxic organic substances from the aqueous environment. The adsorption of
nicotine and its derivatives on DAB and bentonite generally fit to Dubinin-Radushkevich (D-R) equation more than the Freundlich equation.

Recently, adsorption kinetic studies were conducted on flurbiprofen (FBP) (a non-steroidal anti-inflammatory drug) using an organoclay synthesized with tetrabutylammonium (TBA) by Akcay et al. [126]. The authors concluded that the type of adsorption tends to be chemical adsorption, which increases with temperature. The adsorption process is the pseudo-second order and the exothermic nature of the process was reported. The sorption of the FBP on organoclays was well represented by the Freundlich and Dubinin-Radushkevich isotherms and it was seen that the organoclays with TBA was a good adsorbent for FBP due to the high adsorption capacity of organoclays.

Several studies [127-130] have reported the adsorption behaviour of endocrine disruptors such as bisphenol A (BPA) and bisphenyl (BP) from aqueous solution with different materials. Particularly, the study of Cao (2009) showed the potential of organophilic montmorillonite for the removal of BPA. The clay powders were encapsulated with a polyethersulfone (PES) to improve the adsorption capacity. The BPA adsorption data adequately fitted the Langmuir equation and the pseudo-second-order model has been represented well on the equilibrium adsorption data.

2.4 Conclusions
The literature review has shown that there is a strong tendency to use clay minerals such as montmorillonites or bentonites with QACs, and some other non QAC such as polymers, dyes to prepare organoclays. Most of the clay minerals are modified by replacing the organic cations through ion exchange reaction in aqueous solutions. In addition, some difunctional organic cations have been employed for the improvement in the adsorption performance of clays. This has been confirmed by using the modern characteristic tools such as XRD, TGA, FT-IR, and micro analysis. BET as a surface area analyser and UV-Vis spectroscopy also yield useful information on the characteristics of organoclays.

The prepared organoclays have been applied in many different environmental applications, and they are effective as adsorbent materials for the removal of organic
contaminants in surface water and groundwater. Recent papers have reported the effectiveness of organoclays on the uptake of organic contaminants, including aromatic organic compounds, phenolic compounds, pesticides and herbicides. These studies revealed factors that affect the adsorption capacity of organoclays such as variation of pH, temperature, surfactant loadings and mechanisms. Furthermore, thermodynamics and kinetics of adsorption capacity on the organic contaminants have been investigated by many researchers.

2.5 Future studies
In future, the adsorption capacity of organic compounds needs to be improved with the intercalation of different surfactants under various conditions based on previously developed methods. In addition, application of organoclays can be further investigated on the uptake of landfill leachate such as metal cations, herbicides and pesticides, and pharmaceutical and personal care products (PPCPs). Furthermore, there are only a few papers which investigate endocrine disruptor chemicals such as bisphenol A (BPA) and bisphenyl (BP). Therefore, future study on clay minerals as potential adsorbents for the uptake of BPA and BP in aqueous solutions is required.

2.6 References


CHAPTER 3
SYNTHESIS AND CHARACTERISATION
OF ORGANOCLAYS INTERCALATED
WITH HDTMA

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PREFACE

Following the extensive literature review that showed the usefulness of organoclays as adsorbents for the removal of varied organic contaminants, the synthesis of different types of organoclays was undertaken in this investigation in the hope to produce more effective organoclays for the removal of environmental contaminants. It is necessary to understand the changes in the surface properties of montmorillonite (MMT) intercalated with QACs through ion exchange. With respect to the modification of MMT, different concentrations of surfactant are loaded in MMT and the variation of structural configurations within the interlayer space of clays is described in this paper.

Chapter 3 is intended to address a set of objectives about how the surface and structural properties of MMT are influenced by the loading of surfactant, using mainly two characterisation methods, XRD and TG.
STATEMENT OF CONTRIBUTION OF CO-AUTHORS

The authors listed below have certified* that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and
5. they agree to the use of the publication in the student’s thesis and its publication on the QUT ePrints database consistent with any limitations set by publisher requirements.

In the case of this chapter:


<table>
<thead>
<tr>
<th>Contributor</th>
<th>Statement of contribution*</th>
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<tbody>
<tr>
<td>Yuri Park (candidate)</td>
<td>Developed experimental design, conducted experiments, analysed data, and wrote the manuscript.</td>
</tr>
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<td>Godwin A. Ayoko (Principal Supervisor)</td>
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<td>Janos Kristóf</td>
<td>Conducted TG, analysed TG data, and edited the manuscript</td>
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</tr>
<tr>
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<td>Assisted in experimental design, data analysis, and edited the manuscript</td>
</tr>
</tbody>
</table>

Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

[Signature]

Name Signature Date
3.1 Introduction

The abundant clay minerals in nature are widely used in a various range of industries such as nanocomposites, catalysts, photochemical reaction reagents, and adsorbents [1]. Among other applications, clays have extensively been used as adsorbents in environmental applications. However, the clay mineral surface is hydrophilic in nature and this clay surface characteristic makes the natural clays ineffective sorbents for the removal of organic compounds. Such a difficulty has been overcome by introducing cationic surfactant molecules into the interlamellar space, and the properties of clay minerals are enhanced as organoclays. In recent years, organoclays have been used of oil-spill clean-up operations [2-4], and also proposed for the removal of organic contaminants [5-8]. The most commonly used clay for the preparation of organoclays is montmorillonite (MMT) due to its high cation exchange capacity (CEC), swelling properties, high surface areas, and consequential strong adsorption/absorption [9]. The typical 2:1 layered MMT, which consists of two siloxane tetrahedral sheets sandwiching an aluminium octahedral sheet belongs to the swelling group of clays [10]. The swelling clays tend to swell and hydrate upon exposure to water. Because of the isomorphous substitution within the layers (e.g. the replacement of Mg$^{2+}$ or Zn$^{2+}$ for Al$^{3+}$ in the octahedral layer, and Al$^{3+}$ for Si$^{4+}$ in the tetrahedral sheets), the negatively charged clay layer surfaces are counterbalanced by exchangeable cations such as Na$^+$ or Ca$^{2+}$ in the interlayer space.

The intercalation of organic cations such as quaternary ammonium cations (QACs) between clay layers changes the surface properties from highly hydrophilic to increasingly hydrophobic/lipophilic [11]. As followed by the modification of clays with cationic surfactants, basal spacing in the layer increases and new sorption sites of clays are exposed. Such surfactant property changes are highly important for the application of organoclays. In particular, the organoclays are seen to be considerably more effective than untreated clay minerals for the removal of organic contaminants [7, 12]. Furthermore, organoclays based nanocomposites exhibit a remarkable improvement in properties when compared with untreated polymer or conventional micro- and macro-composites [10]. The improvements include increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability. Hence, the industrial applications and improvements are heavily
dependent on the structure and properties of organoclays, which requires to be identified [13].

The application of thermal analysis to study of clays, intercalated kaolinites [14-18], layered double hydroxides [19-22] and nanomaterials [23, 24] is of great significance and is essential for the advancement of knowledge and understanding of clay minerals and their intercalates. In this study, hexadecyltrimethylammonium bromide (HDTMA) is chosen as an example of a long alkyl cationic surfactant for the preparation of organoclays, and the effect of the long alkyl surfactant with different loadings may increase the utilisation of modified clays. This study was also undertaken to investigate the structure of organoclays using X-ray diffraction (XRD) and the interlayer configuration of intercalated surfactant in the MMT was elucidated. Moreover, thermogravimetric analysis (TG) was used to investigate the microenvironment and packing arrangement of organic surfactant within the organoclays. The results obtained in this investigation will offer new insights into the structure and properties of organoclays, and will further lead to potential applications of organoclays in industry applications.

3.2 Experimental

3.2.1 Materials
The pure MMT used in this study was supplied by Sigma-Aldrich as source clay SWy-2-Na-montmorillonite (Wyoming) and this was used without further purification. The cation exchange capacity (CEC) of this montmorillonite is 76.4 meq/100g. The surfactant selected for the organoclay complexes in this study is hexadecyltrimethylammonium bromide (denoted as HDTMA, C₁₉H₄₂BrN, FW: 364.46) from Sigma-Aldrich, and used without any further purification.

3.2.2 Synthesis of organoclays
The synthesis of organoclay complexes was undertaken by the following procedure: 4 g of montmorillonite was initially dispersed in 400 mL of deionised water with a Heidolph magnetic stirrer for about 30 minutes. A predissolved stoichiometric amount of surfactant, which was dissolved in 100 ml of deionised water, was stirred for a further 30 minutes. The dissolved surfactant was slowly added to the clay
suspension at room temperature (about 28 ~ 30 °C). The CEC of the MMT is 76.4 meq/100g, which represents a measure of the loading of the clay with the cationic surfactant. For instance, 1.0 CEC is applied when 76.4 meq/100g is intercalated into the MMT. During the synthesis, a range of surfactant concentration in terms of the CEC value from 0.25 CEC through 2.0 CEC was prepared and labelled as 0.25 CEC-HDTMA, 0.5 CEC-HDTMA, 1.0 CEC-HDTMA, 1.5 CEC-HDTMA, and 2.0 CEC-HDTMA. The mixtures were stirred for 3 hours at room temperature using a Branson Ultrasonic model 250 sonifier with an output of 40 mW. All organoclay products were washed free of bromide anions as determined by the use of AgNO₃, dried at room temperature, and dried further in an oven (at 65 °C) for 12 hr. The dried organoclays were ground in an agate mortar, and stored in a vacuum desiccator for a week.

3.2.3 Characterisation methods

3.2.3.1 XRD
The pure montmorillonite and organoclays were present in stainless sample holders. The powdered X-ray diffraction (XRD) patterns recorded using CuK radiation (λ = 1.5418 Å) on a Philips PANalytical X’Pert PRO diffractometer operating at 40 kV and 40 mA with 0.5° divergence slit, 1° anti-scatter slit, between 3° and 70° (2θ) at a step size of 0.0167°.

3.2.3.2 TG
Thermogravimetric analysis of the modified clays were obtained by using Netzsch TG 209 type Thermobalance at ramp 10 K/min from room temperature to 900 °C in high purity flowing argon (80 %) with 20 % of oxygen. Approximately 7 – 11 mg of finely dried ground samples was heated in an open ceramic crucible.

3.3 Results and discussions

3.3.1 XRD
X-ray diffraction is one of the most important techniques to determine the structural geometry, texture and also identify impurities in layer silicates, which are present in clays. In general, XRD can offer basal spacing information on the organoclays used, which can also provide the molecular structure configuration of surfactants
intercalated in clay layers. The XRD patterns of MMT and organoclays prepared at different surfactant loadings are shown in Figure 3.1. The sodium exchanged MMT has a $d$-spacing of 1.25 nm which has an expansion of 1.40 nm when ion exchanged with 0.25 CEC surfactant concentration level. The expansion at the 0.5 CEC surfactant level results in the expansion of the organoclays to 1.44 nm. Upon increasing the surfactant loading to 1.0 CEC surfactant concentration, $d_{(001)}$ spacing of 1.82 nm was observed. Organoclays with 1.5 CEC surfactant concentration level have the expansion peaks at 1.80 nm, which has a slight smaller peak than that of organoclays with 1.0 CEC surfactant concentration level. The slight decreasing value may be caused by insufficient cationic surfactant added to displace all of the water from the interlayer space. The increasing basal spacing of untreated MMT and organoclays is clearly seen in Figure 3.2. The basal spacing at 2.0 CEC surfactant concentration level reaches of 2.04 nm.

Depending on the concentration of surfactant, HDTMA, the expansion of the layers in each step has been appeared. Based on the results, the configuration structure of molecules between clay unit layers suggested. In 0.25 CEC-HDTMA and 0.50 CEC-HDTMA, the d values are 1.40 and 1.44 nm, respectively, and it implies a lateral monolayer arrangement in the interlayer space of montmorillonite. For 1.0 CEC-HDTMA, it shows a basal spacing at 1.82 nm, which reflecting a lateral bilayer arrangement. At 2.0 CEC-HDTMA, the d basal spacing reaches up to 2.0 nm which reflects a pseudo-trimolecular layer arrangement. This demonstrates the property variation among montmorillonite layers. A model is proposed in which up to 0.5 CEC a surfactant monolayer is formed between the montmorillonitic clay layers, up to 1.0 CEC a lateral bilayer arrangement is formed with excess surfactant adsorbed onto the clay surface, a pseudotrtrimolecular layer is formed at 2.0 CEC with excess surfactant adsorbed onto the clay surface [25]. The loaded surfactant in the interlayer space of MMT has been further investigated by TG.

3.3.2 TG

Thermal stability of organoclays and packing arrangement of organic surfactant within the organoclays at an elevated temperature can be determined by thermogravimetric analysis (TG). Figures 3.3 – 3.7 show the derivative thermogravimetric analyses (DTG) of the organoclays intercalated with surfactant, HDTMA. The results of the analyses of the mass loss and temperature of the mass
Figure 3.1 X-ray diffraction patterns of MMT, HDTMA and organoclays intercalated with HDTMA

Figure 3.2 $d_{(001)}$ spacings of untreated MMT and organoclays intercalated with HDTMA
loss are reported in Table 3.1. The result of untreated MMT without intercalation with the surfactant is noted that there are three mass loss steps at between ambient and 100 °C, second at 135.5 °C, and at 636.3 °C [25]. From the result, the MMT is relatively stable and it begins to lose structural hydroxyl OH units at 636 °C but will maintain the layer structure up to 900 °C [26].

Table 3.1 Results of the TG of untreated MMT and organoclays

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dehydration/Dehydroxylation</th>
<th>Dehydration/Dehydroxylation</th>
<th>De-surfactant</th>
<th>Dehydroxylation/OH unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMT</td>
<td>4.37</td>
<td>-</td>
<td>1.07</td>
<td>135.5</td>
</tr>
<tr>
<td>0.25 CEC</td>
<td>7.17</td>
<td>85</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.5 CEC</td>
<td>3.24</td>
<td>68</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0 CEC</td>
<td>2.14</td>
<td>75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.5 CEC</td>
<td>2.74</td>
<td>63</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.0 CEC</td>
<td>3.30</td>
<td>63</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HDTMA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3.3 TG and DTG of 0.25 CEC-HDTMA
Figure 3.4 TG and DTG of 0.5 CEC-HDTMA

Figure 3.5 TG and DTG of 1.0 CEC-HDTMA

Figure 3.6 TG and DTG of 1.5 CEC-HDTMA
From the Figures 3.3 – 3.7 and Table 3.1, there are several mass loss steps observed. The first two steps of mass loss involve dehydration and/or dehydroxylation from room temperature and before 100 °C. The two steps are attributed to the loss of adsorbed water, and water molecules around metal cations such as Na\(^+\) and Ca\(^{2+}\) on exchangeable sites in MMT. The first mass loss for dehydration/dehydroxylation of adsorbed water varies from 2.14 to 7.17 %. The experimental mass loss during the second hydration and hydroxylation of adsorption water appears only for untreated MMT. The first DTG peak for the desorption of water from the clay is highly intense in 0.25 CEC-HDTMA, and this mass loss peak becomes less with the increase of surfactant concentration loading. The third mass loss step is considered as the removal of surfactant by comparing the peak of pure surfactant. It is noted that the temperature of de-surfactant from organoclays is higher than the boiling temperature of pure surfactant. With the increase of surfactant concentration, the temperature of the third mass loss peak is gradually decreased. From the results, it is concluded that the loading of surfactant affects the de-surfactant mass loss and the temperature is decreased. When the concentration of the organoclay is relatively low (for 0.25 CEC and 0.50 CEC), the organic cations exchanged with Na\(^+\) ions mainly adhere to surface sites via electrostatic interactions. With the increase of surfactant concentration loading to 1.0 CEC, some surfactant molecules tend to attach to the clay surface, which results in the appearance of the peak at 278 °C. When the surfactant loading has exceed over the CEC of clay for 1.5 CEC-HDTMA and 2.0
CEC-HDTMA, the surfactant molecules strongly adhere to clay surface by van der Waals forces, and this causes the peak decreased at 265 and 263 °C, respectively. In addition, the intensity of peak is increased with the increase of surfactant loading. During the de-surfactant procedure, the experimental mass loss increases from 2.91 % (0.25 CEC-HDTMA) to 22.0 % (2.0 CEC-HDTMA), and to 100 % for the pure surfactant. The fourth mass loss over the temperature from 600 to 720 °C is ascribed to the loss of structural hydroxyl groups from within the clay. The intensity of this peak decreases as the increase of the surfactant concentration and at 2.0 CEC-HDTMA, the fourth mass loss step in the DTG curve is almost disappeared.

From the results, it is noted that there are four steps attributed from DTG figures and Table 3.1. The dehydration and/or dehydroxylation of adsorbed water from room temperature involves in the first step, and the second step under 135 °C includes the dehydration or dehydroxylation of water adsorbed by metal cations. The decomposition of surfactant at the temperature between 263 and 338 °C is observed in the third step. In the last step, the dehydroxylation of structural OH units in the clay is observed.

3.4 Conclusions
The organoclays were prepared using MMT and HDTMA as cationic surfactant with long alkyl chain. A combination of XRD and TG is applied in this study to investigate the surfactant loading. Modification of MMT using cationic surfactant into clay interlayer space results in an increase of the total amount of the loaded organic carbon and basal spacings of the organoclays. Based on the basal spacing from the XRD pattern, information of molecular arrangement within the clay interlayer space has been provided as a function of surfactant concentration. The configurations of surfactant within the organoclays take a lateral monolayer arrangement at a lower surfactant concentration (0.25 and 0.50 CEC-HDTMA). The configuration has been changed to pseudotrimolecular layer structure with the increase of surfactant loading at 2.0 CEC-HDTMA. The loading of surfactants into montmorillonite also causes a transformation of clay surface property from hydrophilic to hydrophobic. The loaded surfactant in the interlayer space was further investigated by TG. There are four steps attributed in the DTG. The dehydration and/or dehydroxylation of physically adsorbed water and water molecules around metal cations such as Na⁺ on exchangeable sites in MMT involves in the first two
steps. In the third step, the decomposition of surfactant at the temperature is observed and the intercalated surfactants show higher decomposition temperature when compared to the pure surfactant. The dehydroxylation of structural OH units in the clay is in the last step.

Acknowledgement
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3.5 References


CHAPTER 4
SYNTHESIS AND CHARACTERISATION
OF ORGANOCLAYS INTERCALATED
WITH DDTMA AND DDDMA

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Yuri Park, Godwin A. Ayoko, Janos Kristof, Erzsébet Horváth, and Ray L. Frost,
Thermal stability of organoclays with mono- and di- alkyl cationic surfactants:
1087-1093.
PREFACE
The previous paper demonstrated the structural changes of surfactant within the MMT as a function of surfactant loading using HDTMA. The results confirmed that the interlayer space of the organoclays expanded with an increase in surfactant loadings and it resulted in the presence of different configurations of surfactant molecules within the interlayer space.

In the following chapter, organoclays intercalated with two different types of surfactants (mono- and di-cationic surfactants) were synthesised and the characteristics of the two types of organoclays compared. This is of great importance in the understanding of the effects of different sized surfactants on the surface and structural properties of MMT. The use of XRD and TG techniques is essential in order to elaborate their main structural properties and thermal properties of the organoclays in this study.
STATEMENT OF CONTRIBUTION OF CO-AUTHORS

The authors listed below have certified* that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
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In the case of this chapter:


<table>
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<tr>
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<tr>
<td>Yuri Park (candidate)</td>
<td>Developed experimental design, conducted experiments, analysed data, and wrote the manuscript.</td>
</tr>
<tr>
<td>Godwin A. Ayoko (Principal supervisor)</td>
<td>Assisted in experimental design, data analysis, and edited the manuscript</td>
</tr>
<tr>
<td>Janos Kristóf</td>
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<td>Assisted in experimental design, data analysis, and edited the manuscript</td>
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Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

Prof Godwin Ayoko

Signature

Date 14/10/2013
4.1 Introduction

Clay minerals are abundant in nature and modified clays have received attention in industry as it allows for the creation of new materials with enhanced applicability [1-4]. By replacing the natural exchangeable inorganic cations in the clay minerals with organic cations, modified clay minerals can been prepared and are known as organoclays. These organically modified clays are used in industrial applications such as nanofillers in polymer-clay nanocomposites in order to improve mechanical, thermal and flame retardant properties [5-9]. Apart from polymer-clay nanocomposites, the modified clays can also be used as catalysts, photochemical reaction reagents, rheological modifiers, and adsorbents of environmental contaminants [10-12]. Montmorillonite (MMT) is a commonly used clay. It is a member of smectite group and has exceptional characteristics such as high cation exchange capacity (CEC), swelling properties, high surface area and consequential strong adsorption/absorption [13, 14]. Montmorillonite has a 2:1 structural arrangement, which consists of two siloxane tetrahedral sheets sandwiching an aluminium octahedral sheet. This is a type of clay which swells upon exposure to water. With the isomorphous substitution within the layers, Mg$^{2+}$ or Zn$^{2+}$ for Al$^{3+}$ is substituted in the octahedral layer while Al$^{3+}$ is substituted by Si$^{4+}$ in the tetrahedral sheets. This results in a negatively charged surface. The negatively charged clay surface is counterbalanced by exchangeable cations such as Na$^+$ or Ca$^{2+}$ in the interlayer space of the clay [15].

When the organoclays are intercalated with organic cations such as quaternary ammonium cations (QACs), the surface properties of MMT change from hydrophilic to hydrophobic/lipophilic. The basal spacing and the interlayer spacing in the clay layer relatively increases so that a new sorption site is exposed in the interlayer of the clay. Such surface properties are highly important for the use of organoclays in the environment. In particular, organoclays are considerably more effective than untreated MMT as a filter material [16] and hence, further investigation is required on the structures and properties of organoclays for industrial applications.

In this study, Na-montmorillonite is used to prepare organoclays and two types of cationic surfactants namely: dodecyltrimethylammonium bromide (DDTMA) and didodecyldimethylammonium bromide (DDDMA) are chosen as examples of mono- and di-alkyl cationic surfactants. The organoclays are prepared at different surfactant
loadings as this may increase the utilisation of modified clays. The structural properties and thermal stability of MMT and the organoclays are subsequently identified using X-ray diffraction (XRD) and thermogravimetric analysis (TG) and a comparison between organoclays intercalated with mono- and di-alkyl surfactants were investigated. In particular, TG analysis, which is an essential tool to support microenvironment and packing arrangement of organic surfactant within the organoclays was performed. The obtained results in this study will provide a better insight into the structure and properties of organoclays, which will enhance the potential of organoclays in environmental applications.

4.2 Experimental

4.2.1 Materials

The pure montmorillonite (MMT) used in this study was supplied by Sigma-Aldrich as source clay SWy-2-Na-montmorillonite (Wyoming) and used without further purification. The cation exchange capacity (CEC) of this montmorillonite is 76.4 meq/100 g (according to the specification of its supplier). The surfactants selected for the organoclay complexes in this study are: dodecyltrimethylammonium bromide (denoted as DDTMA, C$_{15}$H$_{34}$NBr, FW:308.34) and didodecyldimethylammonium bromide (denoted as DDDMA, C$_{26}$H$_{56}$NBr, FW:462.64) also from Sigma-Aldrich and used without any further purification.

4.2.2 Synthesis of organoclays

The synthesis of organoclay complexes was undertaken by the following procedure: 4 g of montmorillonite was initially dispersed in 400 mL of deionised water with a Heidolph magnetic stirrer for about 30 minutes. A predissolved stoichiometric amount of the surfactant in 100 mL of deionised water was stirred for 30 minutes. The dissolved surfactant was slowly added to the clay suspension at room temperature (about 28 – 30 °C). The CEC of the montmorillonite, which represents a measure of the loading of the clay with the cationic surfactant is 76.4 meq/100 g. For example, 1.0 CEC is applied when 76.4 meq/100 g is intercalated into the montmorillonite. During the synthesis, a range of surfactant concentrations in terms of the CEC values from 0.25 CEC through 2.0 CEC was prepared and labelled as 0.25 CEC-DDTMA, 0.5 CEC-DDTMA, 1.0 CEC-DDTMA, 1.5 CEC-DDTMA, and 2.0 CEC-DDTMA, and 0.25 CEC-DDDMA, 0.5 CEC-DDDMA, 1.0 CEC-DDDMA,
1.5 CEC-DDDMA, and 2.0 CEC-DDDMA. The mixtures were stirred for 3 hours at room temperature using a Branson Ultrasonic model 250 sonifer with an output of 40 mW. All organoclay products were washed free of bromide anions as determined by the tests with using AgNO₃, dried at room temperature, and dried further in an oven (at 65 °C) for 12 hours. The dried organoclays were ground in an agate mortar and stored in a vacuum desiccator for a week.

4.2.3 Characterisation methods

4.2.3.1 X-ray diffraction

The pure montmorillonite and organoclays were placed in stainless steel sample holders. The powdered X-ray diffraction (XRD) patterns were recorded using CuK radiation (λ = 1.5418 Å) on a Philips PANalytical X’Pert PRO diffractometer operating at 40 kV and 40 mA with 0.5° divergence slit, 1° anti-scatter slit, between 3° and 70° (2θ) at a step size of 0.0167°.

4.2.3.2 Thermogravimetric analysis

Thermogravimetric analysis of the pure montmorillonite was obtained by using TA Instruments Inc. Q500 high-resolution TGA operating at ramp 5 °C/min with resolution 6.0 °C from room temperature to 1000 °C in a high purity flowing nitrogen atmosphere (40 cm³/min). Approximately 7-11 mg of finely dried modified clays were applied for thermogravimetric analysis using Netzsch TG 209 type thermobalance at ramp 10 K/min from room temperature to 900°C in high purity flowing argon (80 %) with 20 % of oxygen.

4.3 Results and discussions

4.3.1 X-ray diffraction

The structural geometry in the layer silicates of clays can be determined by XRD, and this also identifies impurities present in the clay. This technique offers information on the basal spacings of organoclays and this supports the molecular structure configuration of surfactants intercalated within clay layers. The XRD patterns of MMT and organoclays prepared at different surfactant loadings are presented in Figures 4.1 and 4.2. Figure 4.1 shows the XRD patterns of MMT and organoclays intercalated with DDTMA and the patterns of organoclays intercalated with DDDMA are shown in Figure 4.2. The sodium exchanged MMT has a d-
spacing of 1.25 nm was expanded to 1.41 nm when exchanged with DDTMA at 0.25 CEC level. Upon increasing the surfactant loading to 1.0 CEC surfactant concentration, two $d_{(001)}$ spacings of 1.80 and 1.41 nm are observed. On the other hand, the organoclays intercalated with DDDMA at 0.25, 0.5 and 1.0 CEC levels resulted in expansion to 1.53, 1.75 and 1.94 nm. When the surfactant loading reached up to 1.5 CEC, the two $d_{(001)}$ spacings for organoclays intercalated with DDTMA are observed at 1.84 and 1.49 nm, whereas the organoclay intercalated with DDDMA has three d-spacings at 2.14, 1.53 and 1.00 nm. Additionally, at 2.0 CEC-DDDMA, the organoclays have four basal spacings at 1.78, 1.55, 1.17 and 1.03 nm. Thus as the concentration of surfactants (DDTMA and DDDMA) was increased, the expansion of the layers in each step occurred. Such results indicate that the surfactant molecules have more than one molecular arrangement in the montmorillonite interlayer.

The observation of the expansions in basal spacings of the organoclays with the exchange of a monoalkyl cationic surfactant shows that the d values are 1.41 and 1.40 nm in 0.25 CEC-DDTMA and 0.5 CEC-DDTMA, respectively. This implies a lateral monolayer arrangement in the interlayer space of MMT. For 1.0 CEC-DDTMA, a basal spacing at 1.80 nm with a shoulder of 1.41 nm, which represents a lateral bilayer arrangement (with a monolayer) is presented. However, when the organoclays were prepared at 2.0 CEC surfactant level, the basal spacing increased slightly up to 1.84 nm, which reflected a lateral bilayer arrangement. Compared with the exchange of the single cationic surfactant, the use of a dialkyl cationic surfactant (DDDMA) results in several expansions of MMT. For example, at 1.0 CEC level, two expansions at 1.94 and 1.35 nm were observed and these indicate that two structural arrangements of the DDDMA surfactant molecules such as a lateral monolayer and a lateral bilayer occur in the interlayer of the clay. Furthermore, there are three expansions observed at 2.14, 1.53 and 1.00 nm for 1.5 CEC-DDDMA and the large expansion of 2.14 nm reflects a pseudotrimolecular layer arrangement. This variation of property among MMT layers demonstrates that a monolayer is formed between the montmorillonitic clay layers at low surfactant loading (0.25 and 0.5 CEC) and a lateral bilayer arrangement is formed at high surfactant loading up to 2.0 CEC. A pseudotrimolecular layer is only shown when the use of the double chain cationic surfactant, DDDMA at 1.5 CEC with excess surfactant is adsorbed onto the clay surface. Further study of the loaded surfactant in the interlayer space of MMT
has been investigated using thermogravimetric analysis (TG), and this is reported below.

Figure 4.1 X-ray diffraction patterns of MMT and intercalated with DDTMA

Figure 4.2 X-ray diffraction patterns of MMT and intercalated with DDDMA
4.3.2 Thermogravimetric analysis

One method of investigating thermal stability of organoclays and packing arrangement of organic surfactant within the organoclays is to use thermogravimetric analysis (TG) at an elevated temperature. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the organoclays intercalated with the mono- and di-alkyl cationic surfactants, DDTMA and DDDMA are displayed in Figures 4.3 – 4.5.

From the DTG pattern of the MMT (not shown), several mass loss steps were observed. The first two steps of mass loss (up to 200 °C) involve dehydration of water molecules around metal cations such as Na$^+$ or Ca$^{2+}$ on the exchangeable sites in MMT. The last mass loss step at 636 °C was observed and the peak has been assigned to the dehydroxylation of structural OH units in the clays. Such mass loss at high temperature shows that MMT is relatively stable and the structural hydroxyl OH units maintain the layer structure at elevated temperatures.

In the DTG curves of the organoclays intercalated with DDTMA, the first mass loss which is assigned to the dehydration of adsorbed water appeared at 0.25 CEC and the amount of mass loss gradually decreased from 9.04 to 2.92 % when the CEC increased. This result shows that as more surfactant is added into clay, more adsorbed water molecules are replaced. A similar trend is also found in the DTG curves of the organoclays intercalated with DDDMA which have mass loss from 7.75 to 0.97 %. The third peak at 206 – 359 °C is shown for both organoclays and this peak is considered to be the removal of surfactant by comparison with the absence of the peak in MMT. In this step, the temperature of de-surfactant is higher than the decomposition temperature of pure surfactant (at 194 °C and 164/219 °C for DDTMA and DDDMA, respectively). This implies that the surfactant molecules bonded to the MMT siloxane layer requires more heat, and hence, the higher temperature is used to remove the surfactant molecules bonded on the clay surfaces [17]. The de-surfactant temperature is gradually lowered with an increase of the surfactant loading and it becomes closer to the temperature of the pure surfactant.

The amount of mass loss in this third step for organoclays intercalated with DDTMA increases from 2.2 to 9.79 %, whereas the amount of mass loss is significantly increased from 2.09 to 33.13 % for the organoclays intercalated with DDDMA. When the surfactant loading reaches 1.0 CEC, two de-surfactant temperatures are
Figure 4.3 TG and DTG curves of 0.5 CEC-DDTMA (a) and 0.5 CEC-DDDMA (b)

Figure 4.4 TG and DTG curves of 1.0 CEC-DDTMA (a) and 1.0 CEC-DDDMA (b)

Figure 4.5 TG and DTG curves of 2.0 CEC-DDTMA (a) and 2.0 CEC-DDDMA (b)
observed at 263 and 306 °C, and these temperatures are ascribed to the removal of the surfactant (DDTMA) intercalated between the MMT layers. When the surfactant loading is increased to 1.5 CEC, two decomposition temperatures of the surfactant are observed at 266 and 300 °C. For the organoclays intercalated with DDDMA, two de-surfactant temperatures at 272 °C (with a shoulder peak at 170 °C) and 266 °C (with a shoulder peak at 164 °C) are observed at the concentration of 1.5 and 2.0 CEC respectively. The temperature at 170 and 164 °C are close to the decomposition temperature of the pure surfactant and it is ascribed to the decomposition of surfactant bonded to the clay surface while the temperature at 272 and 266 °C can be the decomposition of surfactant bonded on the internal surface of MMT. The last peak for organoclays (as shown in Figures) is assigned to the dehydroxylation of the montmorillonite clay and the structural OH unit within the clay is decomposed at higher temperature. The decomposition temperature of the last peak becomes lower for both organoclays and the intensity is also gradually decreased with increase in the surfactant loading. However, it is found the peaks were not well resolved and this may indicate that not only dehydroxylation of MMT, but also organic surfactant molecules strongly confined within the interlayer space of MMT may be decomposed in the step. Since there is no obvious mass loss calculated for modified clays, it is unlikely to distinguish this mass loss step at high temperature region, and the actual amount of organic molecules is hardly quantified from the mass loss.

To find the actual mass of organic molecules in organic surfactant modified clays, the mass of dry residue is obtained after the samples were heated up to 900 °C. By using this value and knowing the percentage amount of dehydroxylation water from the pure montmorillonite (4.92 %), the amount of MMT in organoclays is calculated and eventually organic matter (DDTMA and DDDMA) is calculated based on a dry basis. The results are summarised in Tables 4.1 and 4.2.

From Tables 4.1 – 4.2, the amount of adsorbed water molecules decreased in the organoclays as the surfactant loading increased. Meanwhile, an increased value of organic molecules is observed. This shows that the prepared organoclays become more hydrophobic. When the concentration of DDTMA reaches 1.0 CEC, there is no change in the ratio of DDTMA/MMT, whereas the ratio of DDDMA/MMT increases with an increase in the surfactant loading.
Table 4.1 The amount of MMT and DDTMA in MMT intercalated with DDTMA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dehydration of H$_2$O /%</th>
<th>Montmorillonite /%</th>
<th>DDTMA /%</th>
<th>Ratio of DDTMA/MMT</th>
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</thead>
<tbody>
<tr>
<td>0.25 CEC</td>
<td>9.04</td>
<td>94.76</td>
<td>5.24</td>
<td>0.06</td>
</tr>
<tr>
<td>0.5 CEC</td>
<td>3.98</td>
<td>90.06</td>
<td>9.94</td>
<td>0.11</td>
</tr>
<tr>
<td>1.0 CEC</td>
<td>2.04</td>
<td>81.81</td>
<td>18.19</td>
<td>0.22</td>
</tr>
<tr>
<td>1.5 CEC</td>
<td>1.95</td>
<td>81.69</td>
<td>18.31</td>
<td>0.22</td>
</tr>
<tr>
<td>2.0 CEC</td>
<td>2.92</td>
<td>81.86</td>
<td>18.14</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Table 4.2 The amount of MMT and DDDMA in MMT intercalated with DDDMA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dehydration of H$_2$O /%</th>
<th>Montmorillonite /%</th>
<th>DDDMA /%</th>
<th>Ratio of DDDMA/MMT</th>
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<tr>
<td>0.25 CEC</td>
<td>7.75</td>
<td>93.35</td>
<td>6.65</td>
<td>0.07</td>
</tr>
<tr>
<td>0.5 CEC</td>
<td>5.18</td>
<td>83.38</td>
<td>16.62</td>
<td>0.20</td>
</tr>
<tr>
<td>1.0 CEC</td>
<td>1.41</td>
<td>72.91</td>
<td>27.09</td>
<td>0.37</td>
</tr>
<tr>
<td>1.5 CEC</td>
<td>1.95</td>
<td>65.38</td>
<td>34.62</td>
<td>0.53</td>
</tr>
<tr>
<td>2.0 CEC</td>
<td>0.97</td>
<td>57.13</td>
<td>42.87</td>
<td>0.75</td>
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</table>

Through the trend of the ratio in Tables 4.1 and 4.2, the correlation between the basal spacings from XRD and the organic loading from TG can be seen. As the organic loading was increased, the basal spacing was also increased. When saturation is reached at and above 1.0 CEC the ratio of MMT and DDTMA remains constant and the basal spacing is constant. However, the basal spacing increases a little further to 1.84 nm from 1.80 nm upon reaching 1.5 CEC. It is suggested that the structural configuration of the surfactant is changed in the interlamellar gallery. For organoclays intercalated with DDDMA, the organic loading was gradually increased as a function of surfactant concentration and the basal spacing was also gradually expanded to 2.14 nm.

From the results, it was noted that the dehydration of adsorbed water or water molecules near metal cations such as Na$^+$ or Ca$^{2+}$ was involved at low temperature (~200 °C). TG analyses of the pure surfactant in powder form shows that DDTMA decomposes at 194 °C and DDDMA decomposes at 164 and 219 °C. The decomposition temperature of both organoclays intercalated with DDTMA and DDDMA was higher than that of pure surfactant. From the decomposition temperatures of the surfactant, it is evident that the surfactant molecules can be
bonded to the external surface of MMT as well as intercalated in the interlayer space of MMT. Additionally, the surfactant strongly confined within the interlamellar gallery is removed at high temperature [18]. Lastly, the dehydroxylation of structural OH units in the MMT takes place at higher temperature, along with the decomposition of a part of the intercalant strongly bonded to the clay internal surface.

4.4 Conclusions
In this work, organoclays have been prepared using Na-montmorillonite and two different types of surfactants, DDTMA and DDDMA as examples of mono- and di-alkyl cationic surfactants. After the surface modification of the MMT, the properties of modified MMT were investigated. As the surfactant loading increased, the basal spacing within the interlayer of the MMT increased and in particular, the interlayer spacing of the organoclays intercalated with DDDMA increased significantly. It was found that two layer arrangements (monolayer and bilayer) are present for the mono-alkyl cationic surfactant (DDTMA) and three layer arrangements (monolayer, bilayer and pseudotrimolecular) are observed for the DDDMA.

The TG results show that the surfactant serves an important function as the decomposition temperature of both surfactant DDTMA and DDDMA was higher than that of pure surfactant (at 194 °C for DDTMA and 164/219 °C for DDDMA) and there are interactions between surfactant molecules and MMT. The mass loss step of MMT dehydroxylation overlapped with the thermal degradation of a part of the intercalant remaining in the interlamellar gallery. Possible explanations for this may be as follows: a part of the reagents is bonded to “superactive” sites of the clay internal surfaces, thus removal of this more strongly bonded molecules occurs at higher temperatures (actually overlapped with the removal of structural OH groups); part of the intercalating organics is partially decomposed to form highly carbonaceous residues, the complete removal (oxidation) of which requires higher temperatures.

It is concluded that larger basal spacings are observed for the organoclays intercalated with DDDMA than organoclays intercalated with DDTMA. This indicates that organoclays intercalated with DDDMA have larger sorption sites, which suggest that they are potentially a better adsorbent for removing organic contaminant [17, 19]. Further studies on the comparative efficiencies of the
organoclays with mono- and di- alkyl cationic surfactants in the removal of organic pollutants are warranted, and such studies as well as those aimed at understanding the adsorption behaviours of the organoclays are underway in this laboratory.

Acknowledgement
Part of this work was supported by the Hungarian Ministry of Culture and Education under grant no. TAMOP-4.2.2-08/1/2008-0018. The financial and infrastructural support of the State of Hungary and European Union in the frame of the TAMOP-4.2.1/B-09/1/KONV-2010-0003 project is gratefully acknowledged. The financial and infra-structure of the Queensland University of Technology, Chemistry discipline is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding some of the instrumentations.

4.5 References


CHAPTER 5
SYNTHESIS AND CHARACTERISATION
OF ORGANOCLAYS INTERCALATED
WITH TDTMA

This paper was originally published:

Yuri Park, Godwin A. Ayoko, and Ray L. Frost, Characterisation of organoclays
and adsorption of p-nitrophenol: Environmental application. Journal of Colloid
PREFACE

The structural configurations of surfactants and thermal properties of the organoclays intercalated with different types of surfactants were described in Chapter 4. It showed, through XRD and TG analyses that the organoclays intercalated with the larger organic cation (DDDMA) tended to have larger basal spacings and appeared to be more thermally stable.

To investigate the physical and chemical properties of organoclays further, various techniques have been applied. In this chapter, the organoclays synthesised with TDTMA at different concentrations of surfactant were characterised by a range of methods, including XRD, surface analyser, infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). These techniques enabled the elucidation of information on the molecular structure, surface area and pore size of the organoclays.

The characterised organoclays were initially used to test their adsorption capacities for the removal of p-nitrophenol. After the adsorption study, the tested organoclays were characterised in terms of the changes in the structural and surface properties of the organoclays that occurred as a result of the adsorption of p-nitrophenol. The obtained results yielded useful information on the mechanisms for the adsorption of the organic molecules.
STATEMENT OF CONTRIBUTION OF CO-AUTHORS

The authors listed below have certified* that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and
5. they agree to the use of the publication in the student’s thesis and its publication on the QUT ePrints database consistent with any limitations set by publisher requirements.

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<tbody>
<tr>
<td>Yuri Park (candidate)</td>
<td>Developed experimental design, conducted experiments, analysed data, and wrote the manuscript.</td>
</tr>
<tr>
<td>Godwin A. Ayoko (Principal Supervisor)</td>
<td>Assisted in the experimental design, provided scientific advice, and edited the manuscript.</td>
</tr>
<tr>
<td>Ray L. Frost* (Associate Supervisor)</td>
<td>Assisted in the experimental design, provided scientific advice, and edited the manuscript.</td>
</tr>
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</table>

Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

[Signature]

Name       Signature       Date

14/10/2013
5.1 Introduction

Clay minerals such as montmorillonite and smectite are abundant in nature. Clay minerals are known as the swelling clays due to their tendency to swell and hydrate upon exposure to water [1]. They are widely used in a variety of industries such as nano composites, catalysts, photochemical reaction reagents, and adsorbents [2]. Among other applications, clays have extensively been used as adsorbents in environmental systems, and the most commonly used clay is montmorillonite because of its high cation exchange capacity (CEC), swelling properties, high surface areas, and consequential strong adsorption/absorption [3, 4]. Montmorillonite (MMT) is a typical 2:1 layered clay mineral that consists of two inward pointing tetrahedral sheets with a central alumina octahedral sheet. The negatively charged clay layer surface is counterbalanced by exchangeable cations such as Na\(^+\) or Ca\(^{2+}\) in the interlayer space due to the isomorphous substitution within the layers (e.g. the replacement of Mg\(^{2+}\) or Zn\(^{2+}\) for Al\(^{3+}\) in the octahedral layer, and Al\(^{3+}\) for Si\(^{4+}\) in the tetrahedral sheets) [4, 5]. Because of the hydration of inorganic cations on the exchange sites, the clay mineral surface is hydrophilic in nature and this makes the natural clays ineffective sorbents for the removal of organic compounds. Such a difficulty has been overcome through ion exchange of inorganic cations with organic cations such as quaternary ammonium cations (QACs), represented as \([(CH_3)_3NR]^+\), or \([(CH_3)_2NR_2]^+\), where R is a relatively short hydrocarbon substitution group.

By introducing cationic surfactant molecules into the interlamellar space through ion exchange, the properties of clay minerals are changed from montmorillonite to organoclays. The intercalation of cationic surfactant between clay layers exchanges the surface properties from highly hydrophilic/lyophobic to increasingly hydrophobic/lipophilic [6]. As a result of the modification of the properties of the swelling clay, the basal spacing in the layer increases and new sorption sites of clays are exposed. Such changes in the properties of the surfactant are important for the application of organoclays, and their significance in hydrophobic organoclay is highlighted by their use for water purification. To date, the application of organoclays to remove various organic compounds has been reported, and relative to untreated clays, the adsorption capacity for the removal organic contaminants has been improved by using organoclays [7-9].
In this study, tetradecyltrimethylammonium bromide (TDTMA) surfactant is used as an example of a long alkyl cationic surfactant for the preparation of organoclays, since the effect of the long alkyl surfactant with different loadings may increase the utilisation utility of the modified clays. The present work was undertaken to investigate the changes of structure and physical properties in the modified clays, and the interlayer configuration of intercalated surfactant in MMT was elucidated by using X-ray diffraction (XRD), transmission electron microscopy (TEM), Brunauer, Emmett, and Teller (BET), thermogravimetric analysis (TG) and Fourier transform infrared spectroscopy (FT-IR). In addition, using X-ray photoelectron spectroscopy (XPS), the surface characteristics of montmorillonite and organoclays were investigated. As many literature articles have reported the effectiveness of organoclays as adsorbents, this study will further investigate any structural or physical changes, or adsorption properties of the resultant organoclays when intercalated with organic compounds. P-nitrophenol was chosen as a test molecule in this research. The obtained results will offer new insights into the structure and adsorption properties of organoclays, and will enhance the potential industrial applications of organoclays as a filter material in water purification.

5.2 Experimental methods

5.2.1 Materials

The pure montmorillonite (MMT) was purchased from Sigma-Aldrich, and was used without further purification. The cation exchange capacity (CEC) of this pure montmorillonite is 76.4 meq/100g (according to the specification of its producer). The surfactant selected for the organoclay complexes in this study is tetradecyltrimethylammonium bromide (denoted as TDTMA, C\textsubscript{17}H\textsubscript{38}NBr, FW: 336.41) from Sigma-Aldrich, and used without any further purification.

5.2.2 Synthesis of organoclays

The synthesis of organoclay complexes was undertaken by the following procedure: 4 g of MMT was initially dispersed in 400 mL of deionised water with a Heidolph magnetic stirrer for about 30 minutes. A predissolved stoichiometric amount of surfactant, which was dissolved in 100 mL of deionised water was stirred for a further 30 minutes. The dissolved surfactant was slowly added to the clay suspension at room temperature (about 28 – 30 °C). The CEC of the MMT is 76.4 meq/100g,
which represents a measure of the loading of the clay with the cationic surfactant. For instance, 1.0 CEC is applied when 76.4 meq/100g is intercalated into the MMT. During the synthesis, a range of surfactant concentration in terms of the CEC value from 0.25 CEC through 2.0 CEC was prepared and labelled as 0.25 CEC-TDTMA, 0.5 CEC-TDTMA, 1.0 CEC-TDTMA, 1.5 CEC-TDTMA, and 2.0 CEC-TDTMA. The mixtures were stirred for 3 hr at room temperature using a Branson Ultrasonic model 250 sonifier with an output of 40 mW. All organoclay products were washed free of bromide anions as determined by the use of the AgNO₃, dried at room temperature, and dried further in an oven (at 65 °C) for 12 hours. The dried organoclays were ground in an agate mortar, and stored in a vacuum desiccator for a week.

5.2.3 Adsorption of p-nitrophenol on the organoclays

0.2 g of the prepared organoclay products were combined with 30 mL of p-nitrophenol solution (4000 mg/L for the adsorption) in 50 mL centrifuged tube with plastic caps. The tubes were shaken for 6 hr at 190 rpm on a shaker at the room temperature. The initial pH of p-nitrophenol is 6.0. After shaking, the mixture was centrifuged at 3500 rpm for 20 minutes. After the centrifugation, the p-nitrophenol concentration in the aqueous phase was determined by a UV-Vis spectrophotometer at 317 nm with a detection limit of 0.05 mg/L.

The p-nitrophenol uptake on MMT and/or organoclays was calculated by the following equation: \[ Q = (C_o - C_e) \cdot V / m \], where \( Q \) is the uptake of p-nitrophenol, \( C_o \) is the initial concentration, \( C_e \) is the equilibrium concentration, \( V \) is the volume of p-nitrophenol solution and \( m \) is the mass of the adsorbent. The losses of the p-nitrophenol by both photochemical decomposition and volatilisation were found to be negligible during adsorption [7]. The obtained MMT and organoclays adsorbed with p-nitrophenol were labelled as MMT-4000, 0.25 CEC-4000, 0.5 CEC-4000, 1.0 CEC-4000, 1.5 CEC-4000 and 2.0 CEC-4000.

5.3 Characterisation methods

5.3.1 X-ray diffraction (XRD)

The pure MMT and synthesised organoclays were pressed in stainless samples holders. Powdered X-ray diffraction (XRD) patterns were recorded using CuKα radiation (\( \lambda = 1.54Å \)) on a Philips PANanalytical X’pert PRO diffractometer.
operating at 40 kV and 40 mA with 0.25° divergence slit, 0.25° anti-scatter between 5 and 15° (2θ) at a step size of 0.0167°. For XRD at low angle section, it was between 1.5 and 8° (2θ) at a step size of 0.0167° with variable divergence slit and 0.125° anti-scatter. In addition, the organoclays adsorbed p-nitrophenol was applied as the same method prior to powder XRD analysis.

5.3.2 Transmission electron microscopy (TEM)
A JEOL 1010/2100 transmission electron microscopy was used to investigate microstructure of organoclays. All samples were ultrasonically dispersed in absolute ethanol solution and a small drops of suspension dissolved in ethanol solution was prepared on carbon-coated films and dried in an oven at 60 °C for 20 mins for TEM studies.

5.3.3 Brunauer, Emmett, and Teller (BET)
With a Micromeritics Tristar 3000 automated gas adsorption surface area analyses based upon N\textsubscript{2} adsorption/desorption were carried out. From the measurement, pore structure parameters were characterised at liquid nitrogen temperature. Before the measurement, the samples were pre-heated at 90 °C under the flow of N\textsubscript{2} on a Micrometrics Flowprep 060 degasser.

5.3.4 X-ray photoelectron spectroscopy (XPS)
The X-ray photoelectron spectroscopy (XPS) was applied using a Kratos AXIS Ultra with a monochromatic Al X-ray source at 225W. A small amount of each fine powdered sample was applied to the double sided adhesive tape on a standard Kratos Axis sample bar. This was attached to the sample rod of the Load Lock system for initial evacuation to 10^{-6} Torr. The sample bar was then transferred to the UHV sample analysis chamber (SAC) for collection of X-ray photoemission spectra. A survey scan was run for each analysis from 0 to 1200 eV with a dwell time of 100 ms, pass energy of 160 eV at step of 1 eV with one sweep. In addition, a high resolution analysis was undertaken at 40 eV at steps of 50 meV. The obtained spectra were analysed using Casa XPS version 2.3.14 software, which enabled the baseline (Shirley baseline applied) and various data handling procedures.

5.3.5 Thermogravimetric analysis (TG)
Thermogravimetric analysis of the pure MMT and synthesised organoclays were obtained by using TA instruments Inc. Q500 high-resolution TGA operating at ramp
5 °C/min with resolution 6.0 °C from room temperature to 1000 °C in a high purity flowing nitrogen atmosphere (40 cm$^3$/min). Approximately 40 – 60 mg of finely dried ground sample were heated in an open platinum crucible.

**5.3.6 Fourier transform infrared spectroscopy (FT-IR)**

Fourier transform infrared spectroscopy (FT-IR) was applied in this work, and the spectra were obtained using a Nicolet Nexus 870 FT-IR spectrometer with a smart endurance single bounce diamond ATR cell. Sixty four scans were collected for each measurement over the spectral range of 550 – 4000 cm$^{-1}$. Spectral manipulation such as baseline adjustment, smoothing, and normalisation were performed by using the GRAMS software package (Galactic Industries Corporation, Salem, NH, USA). Band component analysis was undertaken using the Jandel ‘Peakfit” software package, which enables the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was performed using a Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The peak fitting was produced squared correlation ($R^2$) greater than 0.99.

**5.4 Results and discussion**

**5.4.1 XRD**

XRD is one of the most useful techniques to probe the structural geometry and texture of organoclays. The basal spacing information of organoclays obtained from XRD provides the intercalation and molecular structure configuration of the organic surfactant into the clay layers. The XRD patterns of MMT, and organoclays prepared at different surfactant loadings with and without adsorbed p-nitrophenol are presented in Figures 5.1 and 5.2. The increasing basal spacing of untreated MMT and organoclays is clearly seen Figures 5.3 and 5.4.

The sodium exchanged MMT has a $d$-spacing of 1.25 nm, which was expanded to 1.52 nm upon adsorption of $p$-nitrophenol. This expansion indicated that $p$-nitrophenol is adsorbed between the clay layers. For an ion exchanged of 0.25 CEC surfactant concentration level, a basal spacing of 1.42 nm is observed, and the value of 1.43 nm is observed upon the adsorption of $p$-nitrophenol. The basal spacing of 1.43 nm is observed at the 0.5 CEC-TDTMA and the expansion remains at 1.43 nm after adsorption of $p$-nitrophenol on the 0.5 CEC organoclay. Upon increasing the
Figure 5.1 XRD patterns of MMT, 0.25 and 0.5 CEC with and without adsorbed \( p \)-nitrophenol

Figure 5.2 XRD patterns of MMT, 1.0, 1.5 and 2.0 CEC with and without adsorbed \( p \)-nitrophenol
surfactant loading to 1.0 CEC surfactant concentration, two \( d_{(001)} \) spacings (1.78 and 2.06 nm) are observed, and there are two spacings at 1.52 and 3.10 nm observed upon adsorption of \( p \)-nitrophenol. At 1.5 CEC surfactant concentration level, the organoclays also have the double overlapping expansion peaks at 1.80 and 2.19 nm, which have a slightly more intense peak than that of organoclays at 1.0 CEC surfactant concentration level. Upon adsorption of \( p \)-nitrophenol, the \( d \) spacing changed to 1.60 and 3.22 nm, respectively. The basal spacings at 2.0 CEC resulted in basal spacings of 1.83 and 2.14 nm. Where upon adsorption of \( p \)-nitrophenol, spacings of 1.57 and 3.09 nm are observed. Depending on the concentration of surfactant (TDTMA), the expansion of the layers in each step occurred. Based on the result, the configuration of the structure of the molecules between clay unit layers is suggested.

In 0.25 CEC-TDTMA and 0.5 CEC-TDTMA, the \( d \) values are 1.42 and 1.43 nm, respectively, and this implies monolayer arrangement in the interlayer space of MMT. From 1.0 CEC-TDTMA to 2.0 CEC-TDTMA, the two basal spacings at 1.78 nm (with a shoulder of 2.06 nm), 1.80 nm (with a shoulder of 2.19 nm) and 1.83 nm (with a shoulder of 2.14 nm) indicate the two arrangement of the TDTMA surfactant molecule within the clay mineral layers; the first basal spacing of 1.78 nm, 1.80 nm, and 1.83 nm is attributed to the arrangement of the surfactant molecule within the clay layers either flat or perpendicular to the clay siloxane surface, while 2.06 nm, 2.19 nm, and 2.14 nm basal spacings are ascribed to the surfactant molecules at right angles to the clay mineral surface. Hence, at the higher CEC values from 1.0 to 2.0 CEC, both lateral bilayer and pseudo-trimolecular layer structures of surfactant are observed. Upon adsorption of \( p \)-nitrophenol on the organoclay the basal spacing for untreated MMT was a slight expansion of the clay layers from 1.25 nm to 1.52 nm, while 0.25 CEC-4000 and 0.5 CEC-4000 organoclays both have spacing of 1.43 nm. This unchanged value may suggest that \( p \)-nitrophenol has penetrated and bonded to the surfactant molecules in the clay layers. However, for the 1.0 CEC-4000 organoclays, there are two distinct basal spacings at 1.52 and 3.10 nm. The first spacing of 1.52 nm is assigned to the organoclay with minimal \( p \)-nitrophenol adsorption, while the expansion of 3.10 nm is assigned to surfactant molecules with adsorbed \( p \)-nitrophenol between clay layers. Similar values of basal spacings are also observed upon reaching the 1.5 CEC-4000. By comparison with the previous studies
by Xi et al. [10] and Liu et al. [11] similar configuration changes were obtained. As the surfactant concentration increased, the configuration structure changes from a lateral monolayer to lateral bilayer/pseudotrimolecular layer structure. However, the paraffin layer arrangement was not observed at the higher surfactant concentration in this study, and this may be due to the different molecular sizes of the surfactants. In addition, this result may be affected by the differences in the measurements and in the control humidity.

**Figure 5.3** $d_{(001)}$ spacing of MMT and organoclays

**Figure 5.4** $d_{(001)}$ spacing of MMT and organoclays adsorbed with $p$-nitropheanol
Figure 5.5 TEM images of 0.5 CEC-TDTMA, 2.0 CEC-TDTMA, 0.5 CEC-4000, and 2.0 CEC-4000
5.4.2 TEM
A selection of TEM images of 0.5 CEC-TDTMA, 2.0 CEC-TDTMA, 0.5 CEC-4000, and 2.0 CEC-4000 organoclays are present in Figure 5.5. The images of 0.5 CEC-TDTMA shows that the spacing of 1.44 nm, which is in good agreement with the value of 1.43 nm obtained from XPD data. The 0.5 CEC-4000 shows that the spacing of 1.48 nm, which is slightly bigger than the spacing of 1.44 nm measured by XRD. There are multiple interlayer spacings are found at 2.20, 2.15, 1.85, 1.80 nm for 2.0 CEC-TDTMA. In comparison with the value of 2.14 and 1.83 nm obtained from XRD, there are similar spacings obtained. In addition, upon the adsorption of p-nitrophenol, 2.0 CEC-4000 has also several spacings at 1.32, 1.50, 1.52, 1.78, and 3.02 nm. The observed 3.02 and 1.52 nm are well matched with that of XRD values. Compared to TEM, where various basal spacings were observed, only average were shown by XRD. From the results of the TEM technique, it is proposed that layers are not only linear but also curved or bent. Due to the ununiformed structure, several different interlayer spacings within organoclays are observed.

5.4.3 Surface area measurement
The BET method, the N₂ adsorption-desorption measurements of the clay and organoclays, was used to study the porosity and textual properties at liquid N₂ temperature. The results are shown in Figure 5.6. The Figure indicates that N₂ adsorption isotherms of clay and organoclays exhibit a Type II sorption behaviour in the classification of Brunauer, Deming, Deming and Teller (BDDT) [12]. It is clearly seen that the same form of isotherms and hysteresis loop are seen in both MMT and organoclays. The large uptake of nitrogen is observed close to the saturation pressure, and this apparent step in adsorption branch with a sharp decline in the desorption branch implies the presence of mesoporosity [13-15]. This is in agreement with the pore diameter calculated from the Barrett-Joyner-Halenda (BJH) desorption isotherm as shown in Table 5.1. As shown in Figure 5.6, the adsorption of N₂ of montmorillonite is much higher than that of the other organoclays. This indicates that montmorillonite possesses a higher specific surface area. It is known that the specific surface area (S_{BET}), pore volume (V_p), and pore size distribution can be calculated and the calculated parameters are summarised in Table 5.1.

As shown in Table 5.1, the BET surface area of MMT and organoclays decreases in order: MMT >> 0.5 CEC-TDTMA > 1.0 CEC-TDTMA > 1.5 CEC-TDTMA > 2.0
CEC-TDTMA. Especially, the surface area drops dramatically from MMT to 0.5 CEC-TDTMA. It is also found that the pore volume for organoclays decreases with an increase of loaded surfactants and this will be further discussed using TG results. The pore size is also related to the loading of surfactant, and organoclays with high surfactant loadings have a larger pore size than that with low surfactant loadings. As shown in Table 5.1, using specific surface area and pore volume, there are two different groups made. The surfactant loading concentration up to 0.5 CEC-TDTMA with 23.7631 m$^2$/g and pore volume of 0.086054 cm$^3$/g. The other group includes 1.0 CEC-TDTMA to 2.0 CEC-TDTMA with similar surface area of 8.8507 ~ 10.8419 m$^2$/g and the pore volume of 0.059 ~ 0.065 cm$^3$/g. The organoclays at higher concentrations (1.0 ~ 2.0 CEC TDTMA) have the lower BET surface area and pore volume, whereas MMT has a largest BET surface area and pore volume. From the result, it is assumed that the pore volume and surface area are not a key factor in terms of control the affinity between organoclays and organic pollutants [16]. Hence, the loaded surfactant is highly important to determine the sorption mechanism onto organoclays.

Table 5.1 BET specific surface area ($S_{\text{BET}}$), pore volume ($V_p$) and pore diameter for MMT and organoclays

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$S_{\text{BET}}$/m$^2$/g$^{-1}$</th>
<th>$V_p$/cm$^3$/g$^{-1}$</th>
<th>Mean/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>BET$^b$ BJH$^c$</td>
</tr>
<tr>
<td>MMT</td>
<td>42.71</td>
<td>0.08956</td>
<td>8.364    7.637</td>
</tr>
<tr>
<td>0.5 CEC-TDTMA</td>
<td>23.76</td>
<td>0.08605</td>
<td>14.53    7.243</td>
</tr>
<tr>
<td>1.0 CEC-TDTMA</td>
<td>10.84</td>
<td>0.06535</td>
<td>24.20    8.259</td>
</tr>
<tr>
<td>1.5 CEC-TDTMA</td>
<td>9.432</td>
<td>0.06059</td>
<td>25.77    8.664</td>
</tr>
<tr>
<td>2.0 CEC-TDTMA</td>
<td>8.851</td>
<td>0.05901</td>
<td>26.72    8.746</td>
</tr>
</tbody>
</table>

$^a$ BJH desorption cumulative pore volume of pores between 1.7 and 300 nm in diameter. $^b$ Adsorption average pore diameter (4V/A by BET). $^c$ Barrett-Joyner-Halenda (BJH) desorption average pore diameter (4V/A).
5.4.4 XPS

X-ray photoelectron spectroscopy (XPS) is used to further determine the surface chemical composition and chemical states of prepared materials. This technique has been widely applied for the investigation of top few layers of material surface with partially filled valance band. Figure 5.7 shows the XPS survey scans of montmorillonite, surfactant (TDTMA), and representative organoclays (0.5 CEC-TDTMA and 2.0 CEC-TDTMA). The survey scan has an obvious verification in the presence of sodium, silicon, aluminium, iron, and magnesium in the MMT. It has also indentified the presence of carbon, nitrogen, and bromine in TDTMA. A minor amount of carbon in MMT and oxygen in TDTMA is observed as a result of adsorbed CO$_2$ [17]. The peaks of magnesium and iron (trace amount) are seen in the scans of organoclays, whereas the sodium peak is disappeared. Both magnesium and iron are located in the MMT structure rather than in the interlayer. The absence of
sodium ions in the organoclays confirms the sodium ions are exchanged when cationic surfactants are introduced in the interlayer. The prominent peaks of carbon and silicon are recorded in the MMT and organoclays, the ratio of C/Si has been found and the ratio increased in the following order: 0.34 (MMT) < 1.58 (0.5 CEC-TDTMA) < 1.70 (1.0 CEC-TDTMA) < 1.82 (1.5 CEC-TDTMA) < 2.55 (2.0 CEC-TDTMA). The intercalation of surfactant increases with increased loading. Meanwhile, the Al/Si ratio dropped from 0.42 (MMT) to 0.35 (1.0 CEC-TDTMA) and further 0.34 (2.0 CEC-TDTMA). As the intercalation of surfactants increases in the interlayer, the distance between Al-O(OH) octahedral sheets and two Si-O tetrahedral sheets in the structure of MMT is expanded, and hence, the detecting ratio of Al and Si is lower. This is further investigated by the high-resolution XPS scans.
Figure 5.7 XPS survey scan spectra of MMT, surfactant and organoclays

Table 5.2 Binding energy and their atomic contents of \textit{C} 1s for organoclays

<table>
<thead>
<tr>
<th>C 1s (eV)</th>
<th>0.25 CEC</th>
<th>0.5 CEC</th>
<th>1.0 CEC</th>
<th>1.5 CEC</th>
<th>2.0 CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C bond</td>
<td>281.28 (74.91)</td>
<td>281.34 (72.83)</td>
<td>281.33 (76.09)</td>
<td>281.34 (77.55)</td>
<td>281.38 (84.31)</td>
</tr>
<tr>
<td>C-N bond</td>
<td>283.08 (25.09)</td>
<td>283.09 (27.17)</td>
<td>283.04 (23.91)</td>
<td>283.08 (22.45)</td>
<td>283.09 (15.69)</td>
</tr>
</tbody>
</table>
The high resolution XPS spectra of O 1s of MMT and organoclays are compared in Figure 5.8. It hardly distinguishes between O and OH in the MMT. The intense main peak with the binding energy of 529.42 eV corresponds to O(OH) in the MMT structure, while the other small peak at 531.17 eV is considered as oxygen in H2O. The small trace of an oxygen peak is not observed in organoclays due to their hydrophobic characteristics and the binding energy has decreased from 528.64 to 527.59 eV when the surfactant loading increased from 0.5 to 2.0 CEC. This reduced binding energy is also observed in the high resolution Si 2p and Al 2p spectra (Figure 5.9). The decreased binding energy of both O 1s and Si 2p shows the change of interlayer structure in organoclays.

In the high resolution XPS spectra, C 1s of organoclays is characterised by two transitions at 281 and 283 eV (Figure 5.10). The transition peak at about 281 eV is ascribed to the C-C bond in the long chain of the surfactant, and the C-N bond has a binding energy of about 283 eV. Table 5.2 shows the results for curve fitted binding energy and their atomic contents (at. %) of the highly resolved C 1s XPS spectra present in Figure 5.10. The binding energy for C-C bond increases gradually as the surfactant loading increases from 0.25 to 2.0 CEC in organoclays, while C 1s binding energy of C-N bonds remain similar. The result of C 1s binding energy for C-C bond shows that the loading surfactant affects the C 1s binding energy in organoclays. When the cationic surfactant is intercalated in the interlayer structure, the nitrogen as a head group in the alkyl surfactant interacts with the negative clay due to the electrostatic interaction. From the interaction between nitrogen head group and negative clay surface, the binding energy for C-N remains similar and the binding energy is not changed with an increase of the loading surfactant. However, the increasing binding energy for C-C bond may be explained by the arrangement of surfactant in the interlayer. At the lower concentration of the surfactant, the alkyl chains are parallel to the silica clay surface within the interlayer (e.g. monolayer or bilayer). As a result of an increase amount of loading surfactant, the arrangement of surfactant is at right angle to the clay mineral surface such as pseudo-trimolecular or paraffin structures, which can be described using XRD. The increased packing density within the interlayer causes the increase of C-C binding energy in the alkyl chain. Bromide peaks were observed from the scan of the organoclays. However, the highly well resolved Br peaks are poorly obtained (not shown) and the content of
bromine in organoclays is limited. The result indicates that the preparation of organoclays, which are free of Br ions was successful and that the surfactant TDTMA$^+$ was highly exchanged with Na$^+$ within the interlayer [18, 19].

Figure 5.8 XPS high resolution spectra of O 1s for MMT (a) and organoclays (b and c)
Figure 5.9 XPS high resolution spectra of Si 2p and Al 2p for MMT (a and d) and organoclays (b, e and c, f)
Figure 5.9 (continued)
Figure 5.10 XPS high resolution spectra of C 1s for organoclays (a – c)
5.4.5 TG

Thermal stability of organoclays and packing arrangement of organic cationic surfactant within the organoclays at an elevated temperature were determined by TGA [4, 20, 21]. The TG and DTG curves for MMT and the organoclays with and without p-nitrophenol are shown in Figures 5.11 and 5.12.

In Figure 5.11, there are several mass loss steps observed. The first two mass loss steps of MMT involve dehydration and/or dehydroxylation from room temperature and before 110 °C. The two steps are attributed to the dehydration of adsorbed water, and water molecules around metal cations such as Na⁺ or Ca²⁺ in the exchangeable sites of MMT. The experimental mass loss peak during the second hydration and hydroxylation of adsorption water appears only for untreated MMT and 0.25 CEC-TDTMA. The MMT (Figure 5.11(a)) shows two thermal decomposition steps at both 483 and 611 °C, which were caused by the dehydroxylation of the MMT. The decomposition at a lower temperature 483 °C is assigned to the loss of OH units at the end of clay layers, while the temperature at 611 °C is contributed by dehydroxylation of clay. However, the thermal decomposition of MMT with adsorbed p-nitrophenol is differently shown. Figure 5.12(a) shows that the decomposition at 287 °C is occurred and this may be assigned to the adsorbed p-nitrophenol on MMT. It is reported by Zhou and colleagues that p-nitrophenol sublimes at 131 °C [22]. The reason for obtaining higher temperature than 131 °C may be chemical reactions between the adsorbed p-nitrophenol and clay surface of MMT.

One small dehydration peak for 0.25 CEC-TDTMA and 0.5 CEC–TDTMA is observed at 373 and 369 °C, respectively. Meanwhile, there are three peaks centred at 189/255/370 °C for 1.0 CEC-TDTMA, 184/253/370 °C for 1.5 CEC-TDTMA, and 183/246/371 °C for 2.0 CEC-TDTMA. The third step is considered as the loss of surfactant by comparing the peak of pure surfactant, which decomposes at 194 °C, with that of untreated MMT. From the results, it is proposed that the number of peaks in the third step is affected by the loading of the surfactant. When the concentration of the organoclay is relatively low (e.g. 0.25 CEC and 0.5 CEC), there is a single peak observed (the peak position around 370 °C). The reason for the single peak is that the organic cations exchange with Na⁺ ions, which is mainly adhered to the surface sites via electrostatic interactions [21].
(a) Montmorillonite

(b) TDTMA

(c) 0.25 CEC-TDTMA
(d) 0.5 CEC-TDTMA

(e) 1.0 CEC-TDTMA

(f) 1.5 CEC-TDTMA
With the increase of surfactant concentration loading, some surfactant molecules tend to attach to the clay surface, which results in the appearance of the second peak (the peak position around 250 °C). When the surfactant loading has exceeded the CEC of the clay (1.0, 1.5 and 2.0 CEC), the surfactant molecules strongly adhere to the clay surface by Van der Waals forces, and this causes a new peak to appear (at 183 – 185 °C). In addition, the intensity of the peaks increase with increased surfactant loading. The effect causes the temperature of the decomposition surfactant in the third step to increase. The second and third peaks for 1.0 CEC-TDTMA, 1.5 CEC-TDTMA, and 2.0 CEC-TDTMA compare closely to the pure surfactant peak at 194 °C, and the temperature of the two peaks is gradually decreased.

The thermal decomposition peaks for organoclay with adsorbed p-nitrophenol are observed in Figure 5.12. The two decomposition peaks of 0.25 CEC-4000 are observed at 254 and 374 °C. The formal is attributed to the adsorbed p-nitrophenol on organoclay, while the later decomposition temperature is ascribed to the combustion of the surfactant. The thermal decomposition of 0.5 CEC-4000 is very different from that of the organoclay. The main difference is the presence of two peaks for the loss of adsorbed p-nitrophenol. Two thermal decomposition steps at 196 and 271 °C are observed with mass losses of 2.66 and 0.84 % and these may be
formed from the result of the removal and desorption of \( p \)-nitrophenol in the clay layers [22]. The mass loss at 367 °C of 9.87 % is the loss of the surfactant. When the surfactant loading is increased above 0.5 CEC, three decomposition steps are observed for 1.0, 1.5, and 2.0 CEC adsorbed \( p \)-nitrophenol. The three decomposition temperatures are 174, 224, and 368 °C for 1.0 CEC-4000, 173, 222, and 369 °C for 1.5 CEC-4000, and 174, 221, and 369 °C for 2.0 CEC-4000. The first two decomposition steps are assigned to the loss of surfactant, and the later decomposition temperature is attributed to the loss of intercalated surfactant molecules. The adsorbed \( p \)-nitrophenol peaks, which were found at 0.25 and 0.5 CEC, are not observed, and this is assumed that the adsorbed \( p \)-nitrophenol is decomposed simultaneously with the surfactant. During the desurfactant procedure, the experimental mass loss increases from 6.23 % (0.25 CEC-TDTMA) to 20.46 % (2.0 CEC-TDTMA), and 100 % for the pure surfactant. The last mass loss over the temperature from 611 to 584 °C is ascribed to the loss of hydroxylation from the structural inner OH units of the MMT.

The dehydroxylation temperature in the organoclays upon the adsorption of \( p \)-nitrophenol is lower because of the chemical reaction between adsorbed \( p \)-nitrophenol and siloxane clay surfaces. The chemical binding of the \( p \)-nitrophenol to the inner OH units reduces the dehydroxylation temperature. The intensity of the peak decreases with increase in the surfactant concentrations.

It is summarised that four steps are discernible from DTG figure (Figures 5.11 – 5.12, and Table 5.3). The first two steps involve the dehydration and/or dehydroxylation of adsorbed water and water adsorbed by the metal cations. The decomposition of the surfactant at the temperature between 184 and 373 °C is observed in the third step. Upon the adsorption of \( p \)-nitrophenol, the decomposition of adsorbed \( p \)-nitrophenol is determined and the organoclays above 0.5 CEC, \( p \)-nitrophenol is decomposed simultaneously with the surfactant. In the last step, the dehydroxylation of OH structural units in the clay is observed at the temperature from 611 to 584 °C. It is noted that the temperatures for the loss of \( p \)-nitrophenol are relatively greater than that for the pure \( p \)-nitrophenol, and this indicates the \( p \)-nitrophenol molecules are strongly bonded to the organoclay, which leads to lower dehydroxylation temperature.
(a) Montmorillonite-4000

(b) 0.25 CEC-4000

(c) 0.5 CEC-4000
Figure 5.12 Thermogravimetric analysis of MMT and organoclays adsorbed p-nitrophenol
Table 5.3 TG results of MMT, surfactant (TDTMA) and organoclays and organoclays adsorbed $p$-nitrophenol

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dehydration/Dehydroxylation</th>
<th>Dehydration/Dehydroxylation</th>
<th>De-surfactant</th>
<th>Dehydroxylation/OH unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMT</td>
<td>10.78</td>
<td>1.34</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>0.25 CEC</td>
<td>7.81</td>
<td>2.29</td>
<td>108</td>
<td>-</td>
</tr>
<tr>
<td>0.5 CEC</td>
<td>6.00</td>
<td>2.87</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0 CEC</td>
<td>3.67</td>
<td>3.67</td>
<td>-</td>
<td>-</td>
</tr>
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- Mass loss of adsorbed $p$-nitrophenol
- Thermal decomposition of adsorbed $p$-nitrophenol
- Mass loss of adsorbed $p$-nitrophenol and surfactant
- Thermal decomposition of adsorbed $p$-nitrophenol and surfactant
5.4.6 FT-IR

Infrared spectroscopy is an essential method to probe the molecular environment of the intercalated surfactant for the organoclays [23]. From the observed infrared spectra, there are several distinct regions: OH stretching region (3700 – 3000 cm\(^{-1}\)), CH stretching region (2900 – 2800 cm\(^{-1}\)), HOH bending vibration region (1700 – 1600 cm\(^{-1}\)) and HCH bending vibration region (1520 – 1400 cm\(^{-1}\)).

5.4.6.1 OH stretching region

As shown in Figure 5.13, the infrared spectrum of MMT and organoclays (a) and adsorbed with \(p\)-nitrophenol (b) in the OH stretching region is characterised by two bands at 3700 – 3000 cm\(^{-1}\).

![Figure 5.13 IR spectra of MMT and organoclays with and without adsorbed \(p\)-nitrophenol in 3900 – 3000 cm\(^{-1}\) spectral range](image-url)

**Figure 5.13** IR spectra of MMT and organoclays with and without adsorbed \(p\)-nitrophenol in 3900 – 3000 cm\(^{-1}\) spectral range
A sharp and intense peak at 3631 cm\(^{-1}\) for MMT is assigned to OH stretching vibrations of the structural hydroxyl group, while the broad bands at 3402, 3330, and 3230 cm\(^{-1}\) are ascribed to other water hydrogen bonded to water molecules adsorbed within the interlayer of the clay (see Figure 5.13a). The infrared spectrum of MMT with adsorbed \(p\)-nitrophenol shows peaks in similar position to that of non-reacted MMT (see Figure 5.13b). The bands at 3421, 3347, and 3243 cm\(^{-1}\) for MMT-4000 shows an increased intensity than that of MMT. However, the bands for water hydrogen bonded to other water molecules no longer existed when the surfactant loading has exceeded the CEC of the clay. This is in great agreement with the study by Zhou et al. There is a hydrogen bond between \(p\)-nitrophenol with water for untreated MMT and organoclays at low CEC concentrations [6].

The position of the sharp band corresponding to the OH vibrations of the structural hydroxyl groups is relatively independent of the surfactant concentration. However, the broad bands between 3500 – 3200 cm\(^{-1}\) are strongly dependent on the surfactant concentration loading. At low concentrations of surfactant, the infrared spectrum of 0.25 CEC-TDTMA showed the broad adsorption band near 3382 cm\(^{-1}\) with shoulders at 3578 and 3255 cm\(^{-1}\). The band shifted to lower wavenumber from 3382 to 3364 cm\(^{-1}\) with an increase in the surfactant loading up to 1.0 CEC-S. The change in wavenumber is related to the environment of water. In addition, additional bands at 3672 and 3700 cm\(^{-1}\) are observed above 1.0 CEC-TDTMA and this is suggested that the water in the montmorillonite is gradually displaced with the surfactant (TDTMA), and that the surfactant is adsorbed on other surfactant molecules, which have already been adsorbed in the clay interlayer.

5.4.6.2 CH Stretching region

The spectra of the CH stretching region for MMT and organoclays at different surfactant loadings and with \(p\)-nitrophenol are shown in Figure 5.14. No bands attributable to the CH stretching vibrations were observed for MMT and MMT-4000. However, infrared bands in the region between 2700 and 2900 cm\(^{-1}\) are observed for organoclays modified with TDTMA, and these are ascribed to the antisymmetric \(\nu_{as}(CH_2)\) and symmetric \(\nu_{s}(CH_2)\) stretching modes of the surfactant. It is observed that the CH\(_2\) asymmetric stretching modes slightly shifted to lower wavenumbers upon intercalation of the surfactant molecules (from 2927 to 2925 cm\(^{-1}\)). The wavenumber of the symmetric CH\(_2\) stretching modes is shifted to 2848 cm\(^{-1}\) from
2853 cm\(^{-1}\). From the spectra, the wavenumbers of the antisymmetric and symmetric CH stretching modes of amine chains in the region indicated the conformational difference between organoclays intercalated with TDTMA at the various CEC concentrations. Li and Ishida [24] reported that the chains are highly ordered (all-trans conformation), the wavenumbers are decreased with in accordance to the increase of ordered conformers within the clay interlayers. Similarly, the antisymmetric and symmetric CH stretching modes shifted to low wavenumbers for organoclays adsorbed with \(p\)-nitrophenol.

It is suggested that these two CH stretching peaks are extremely sensitive to the conformational changes of the chain within the interlayer, where the wavenumber decreases as the loading of the surfactant increase from 0.25 to 2.0 CEC. Similar results have been shown in some previous studies [25, 26]. Thus the wavenumbers of the CH stretching bands are highly sensitive to the conformational changes of the
chain, which can be qualitatively monitored by the wavenumber shifts. In addition, a significant wavenumber shift indicates more gauche conformational molecules introduced into alkyl chain with the decrease of alkyl chain length. The conformation of adsorbed long alkyl chain surfactants progressively forms a solid like molecular environment (with high packing density and ordering), and this increase in surfactant packing density can lead to the expansion of clay mineral interlayer spaces, which can be characterised by XRD.

5.4.6.3 HOH and HCH banding vibrations

Figure 5.15a presents the changes in the adsorption bands related to the HOH bending vibrations of the water molecules adsorbed on MMT and organoclays. The positions at these bands for montmorillonite are at 1631 cm\(^{-1}\) with a shoulder at 1654 cm\(^{-1}\). It is apparent from Figure 5.15a that the wavenumber of the water bending peaks shifted significantly to higher wavenumbers from 1630 cm\(^{-1}\) with the increase in surfactant concentration. However, the intensity of this adsorption band decreased, and this can be attributed to the level (e.g. 2.0 CEC-TDTMA) is less than that at lower surfactant concentrations (e.g 0.25 CEC-TDTMA).

The IR spectra of MMT and organoclays with adsorbed \(p\)-nitrophenol are shown in Figure 5.15b. The HOH bending modes for MMT-4000 are observed at 1627 cm\(^{-1}\) with a shoulder of 1653 cm\(^{-1}\). An additional small peak at 1594 cm\(^{-1}\) appears, and this is assigned to adsorbed \(p\)-nitrophenol compared to the spectra of non-reacted MMT. From the literature \([6]\), the peak at 1599 cm\(^{-1}\) is ascribe to C=C aromatic stretching vibration, and the OH deformation modes of \(p\)-nitrophenol is present at 1623 cm\(^{-1}\). The wavenumber of OH bending peaks of organoclays with adsorbed \(p\)-nitrophenol are gradually shifted from 1627 cm\(^{-1}\) to 1613 cm\(^{-1}\) with an increase of loading surfactant. The intensity of the water bending modes is gradually decreased with the increase of surfactant loading, whereas the intensity of \(p\)-nitrophenol at 1594 cm\(^{-1}\) is significantly increased. It is proposed that \(p\)-nitrophenol is highly reacted with clay surface in the organoclays, and that as a result of the intercalation of the surfactant, the surface property of MMT is modified from hydrophilic to hydrophobic.

Major peaks in the region between 1360 and 1560 cm\(^{-1}\) appeared to be due to the methylene scissoring modes and the HCH deformation region of the TDTMA intercalated MMT as shown in Figure 5.16a.
Figure 5.15 IR spectra of MMT and organoclays with and without adsorbed \( p \)-nitrophenol in the 1720 – 1560 cm\(^{-1} \) spectral range

Figure 5.16 IR spectra of MMT and organoclays with and without adsorbed \( p \)-nitrophenol in the 1560 – 1360 cm\(^{-1} \) spectral range
The bands in this region for MMT are found at 1506, 1480, 1451, and 1420 cm\(^{-1}\). However, the band at 1506 and 1420 cm\(^{-1}\) are not observed in the surfactant intercalated with MMT. At low CEC surfactant concentration (0.25 CEC-TDTMA), two small peaks at 1487 and 1475 cm\(^{-1}\) appeared and the intensity of these peaks increases with increase in the surfactant loading. The IR spectra of MMT and organoclays with adsorbed p-nitrophenol are shown in Figure 5.16b. The peak at 1515 cm\(^{-1}\) in MMT is drawn by the adsorbed p-nitrophenol as antisymmetric NO\(_2\) stretching vibrations (at 1523 cm\(^{-1}\)). The wavenumber from 1523 cm\(^{-1}\) to 1515 cm\(^{-1}\) provides again a strong evidence for the reaction between p-nitrophenol with the clay surfaces of MMT. The intensity of peaks at 1498, 1488, 1475, and 1461 cm\(^{-1}\) increases with increase in the surfactant loading.

### 5.4.7 Adsorption of p-nitrophenol on organoclays

The prepared MMT and organoclays are used for the adsorption study of p-nitrophenol in water, and the results are given in Figure 5.17. The adsorbed amounts of p-nitrophenol onto MMT and organoclays increase in order: MMT < 0.25 CEC-TDTMA < 0.5 CEC-TDTMA < 1.0 CEC-TDTMA < 1.5 CEC-TDTMA < 2.0 CEC-TDTMA. The amount of adsorbed p-nitrophenol on organoclays is larger than that on MMT. It is also found that the addition of surfactants is in organoclays would increase the amount of adsorbed p-nitrophenol on organoclays. Therefore, the amount of loaded surfactant is important factor to determine the adsorbed amount of p-nitrophenol onto organoclays.

From the characterisation studies of MMT and organoclays, the mechanisms of adsorbed p-nitrophenol are suggested. MMT has mainly electrostatic attraction between p-nitrophenol and hydrated cations in interlayer space of the clay and therefore, the larger \(d\)-spacing is observed in XRD pattern [27]. As the loaded surfactant molecules in the interlayer space of clay, the surface properties for organoclays convert from hydrophilic to hydrophobic and the intercalated surfactant molecules are also sorbed outside the clay layer. From the study of BET, there are two groups of organoclays observed. For organoclays prepared at relatively low surfactant loadings (0.25 and 0.5 CEC), surfactant molecules are preferred to intercalated in the interlayer space of clays, hence, p-nitrophenol molecules have adsorbed in the interlayer space of organoclays and the organoclays intercalated with surfactant molecules are an excellent medium for partition of p-nitrophenol [16].
However, organoclays prepared at surfactant loadings exceed 1.0 CEC, surfactant molecules are highly intercalated in the clay interlayer space as well as inter-particle pores, which lead to decreased surface area and pore volume. Hence, the clay layers are almost completely enclosed, and the pores are enlarged by the loaded surfactant molecules. The $p$-nitrophenol molecules can be captured not only within the clay layer space but also in the enlarged pores. The organoclay as a partition medium has strong affinity on $p$-nitrophenol molecules [28] and its efficiency is shown in the adsorption curves in Figure 5.17.

Accordingly, the sorption efficiency of the corresponding organoclays is higher than MMT. Based on the distribution and arrangement of surfactant in organoclays, the mechanism is suggested as: the sorption mechanism of organic molecules at the organoclays (1.0 CEC – 2.0 CEC) is controlled by partition, whereas the organoclays prepared at lower surfactant loadings are mainly adsorption [8, 29-31].

![Figure 5.17 Uptake of $p$-nitrophenol by MMT and organoclays](image.png)
5.5 Conclusions

Organoclays were prepared using MMT and tetradecyltrimethylammonium bromide (TDTMA) as an example of a surfactant with a long alkyl chain. The prepared organoclays were characterised by modern physical techniques. Based on the basal spacing from the XRD pattern, information of the molecular arrangement within the clay interlayer space has been obtained as a function of the surfactant concentration. The configurations of the surfactant within the organoclays take a lateral monolayer arrangement at lower surfactant concentration (0.25 and 0.5 CEC). At higher surfactant concentrations (1.0 – 2.0 CEC), both configurations of the surfactant (a lateral bilayer and pseudotrimolecular layer structures) were observed. Moreover, the XRD pattern of organoclays adsorbed p-nitrophenol indicated the intercalation of p-nitrophenol within organoclays, and the expanded interlayer spacing of organoclays were measured and identified using TEM. Using BET method, it is found that the surface area is inversely related to the pore volume for organoclays. As the loading of the surfactant increase in organoclays, the pore size becomes smaller with an increase of surface area. Hence, it is concluded that the pore parameters are significantly related to the distribution and arrangement of surfactant intercalated into the clay surface. The loaded surfactant in the interlayer space were further analysed by TGA. Throughout the XPS study, the chemical composition of MMT and organoclays were analysed and the binding energy of C-C is relatively sensitive to determine the structural changes in organoclays. In infrared spectra, the CH stretching region was extremely sensitive to conformation changes of the chain within the interlayer and a significant wavenumber shift indicates that more gauche conformational molecules introduced into alkyl chain with the decrease of alkyl chain length. From the results, the structural properties of organoclays intercalated with surfactant were changed from hydrophilic to hydrophobic, and the adsorbed p-nitrophenol intercalates the organoclay and displaces the surfactant molecules or rearranges the structure of surfactant molecules within the organoclay interlayer. In addition, the different sorption mechanisms involving adsorption and/or partition may affect the sorption of p-nitrophenol onto organoclays. This type of organoclays will potentially be used as good adsorbents for recalcitrant organic molecules in the industry and this organoclay will be applied to test in adsorbing efficiency from p-nitrophenol and further removal of herbicides and pesticides from contaminated samples.
Acknowledgement

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5.6 References


CHAPTER 6
APPLICATION OF ORGANOCLAYS FOR
THE ADSORPTION OF PHENOLIC
COMPOUNDS I

This paper was originally published:

The previous paper had demonstrated the structural and surface properties of organoclays intercalated with TDTMA and their potential as adsorbents for the removal of p-nitrophenol.

Considering the structural and thermal properties of organoclays intercalated with HDTMA (Chapter 3), DDTMA and DDDMA (Chapter 4), and TDTMA (Chapter 5), and the larger basal spacings observed in the interlayer space of organoclays intercalated with the larger organic cations, the following chapter set out to explore the ability of the new adsorption sites observed in the previous chapters.

Three different types of organoclays intercalated with HDTMA, DDTMA and DDDMA are tested and a comparison of their adsorption efficiencies for the removal of organic contaminants is made. Since HDTMA and TDTMA are similar in size, it was proposed that the adsorption efficiencies of organoclays intercalated with HDTMA and TDTMA would not be expected to have significant differences. Hence, the use of three different types of organoclays (MMT-HDTMA, MMT-DDTMA and MMT-DDDMA) was undertaken to provide further information on the comparative adsorption efficacies of the organoclays for organic pollutants from aqueous solutions.

This chapter and paper examined the conformational changes of HDTMA cations in the interlayer space through MM calculation and the simulation models enhanced a visual understanding of the results from characterisation methods. The results described in the chapter have applications in the removal of phenolic compounds (e.g. p-nitrophenol and p-chlorophenol). Different experimental conditions were applied in order to determine the optimum sorption. The obtained results explained the mechanisms involved in the adsorption of phenolic compounds and promoted the potential uses of organoclays.
STATEMENT OF CONTRIBUTION OF CO-AUTHORS

The authors listed below have certified* that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and
5. they agree to the use of the publication in the student's thesis and its publication on the QUT ePrints database consistent with any limitations set by publisher requirements.

In the case of this chapter:

Structural characterisation and environmental application of organoclays for the removal of phenolic compounds. Journal of Colloid and Interface Science 393 (2013) 319-334

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<td>Developed experimental design, conducted experiments, analysed data, and wrote the manuscript.</td>
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<td>(candidate)</td>
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<tr>
<td>Godwin A. Ayoko*</td>
<td>Assisted in the experimental design, supervised and provided scientific advice, and edited the manuscript.</td>
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<td>(Principal Supervisor)</td>
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<tr>
<td>Erzsébet Horváth</td>
<td>Developed computational modelling, interpreted data, and aided in presentation of the computational modelling data</td>
</tr>
<tr>
<td>Róbert Kurdi</td>
<td>Developed computational modelling, interpreted data, and aided in presentation of the computational modelling data</td>
</tr>
<tr>
<td>Janos Kristof</td>
<td>Developed computational modelling, interpreted data, and manuscript editing</td>
</tr>
<tr>
<td>(Associate Supervisor)</td>
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<tr>
<td>Ray L. Frost</td>
<td>Assisted in the experimental design, supervised and provided scientific advice, and edited the manuscript</td>
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</table>

Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

PROF GODWIN AYOKO

Name  Signature  Date

14/10/2013
**6.1 Introduction**

The world is facing formidable challenges in the remediation of toxic contaminants from industrial effluents [1-4]. In particular, phenolic compounds are one of the main pollutants found in the water as a result of industrial discharges. Since they are harmful to living organisms even at low concentrations, they are considered as the priority pollutants [5]. There has been increasing interest in the development of innovative and promising adsorbent materials that will resolve the problem of industrial wastewater pollution [6-9]. Of the materials that are available, natural clays such as montmorillonite are extensively used as adsorbents due to their high cation exchange capacity (CEC), swelling properties, and high surface areas [10]. Montmorillonite (MMT) is a 2:1 type clay mineral which possesses two silica-oxygen tetrahedral sheets with a central alumina octahedral sheet (TOT layer). The isomorphic substitution within the layers (i.e. Al\(^{3+}\) replaced by Mg\(^{2+}\) or Fe\(^{2+}\) in the octahedral sheet, Si\(^{4+}\) replaced by Al\(^{3+}\) in the tetrahedral sheets) causes the surface of the clay layer to be charged negatively, which is counterbalanced by exchangeable cations (e.g. Na\(^{+}\) or Ca\(^{2+}\)) in the interlayer space. Because of the hydration of inorganic cations the clay surface is hydrophilic. This makes clay minerals to be ineffective adsorbents for the removal of organic compounds [11, 12]. In recent years, more attention has been drawn to the development of modified clays such as organoclays to improve adsorption capacities of clays. By replacing of inorganic cations with organic ones such as quaternary ammonium cations (QACs) in the interlayer space, hydrophilic clays are converted to hydrophobic organoclays [13-17]. This is a key strategic step in the improvement of the adsorption capacity for the removal of organic pollutants.

Many studies have reported that organoclays are widely used in various industrial areas, particularly, as adsorbents for organic pollutants and airborne organic contaminants [18-21]. From previous studies [22, 23], different sorption mechanisms are demonstrated and they are highly associated with the molecular structure of organic pollutants and QACs in the modified clays. The adsorption behaviour of organoclays prepared by different types of surfactant (small or large organic cations) creates different adsorption mechanisms and it affects significantly the adsorption capacity of organoclays [24, 25]. Not only the size of alkyl chain length but also the charge density of the clay layer is incorporated in the adsorption capacity of
organoclay. This means that the charge density of the clay layer is responsible for the arrangement of intercalated organic cations within the interlayer of clay which controls the adsorption capacity of organoclay. To the best of our knowledge, only few studies have attempted to describe the arrangement of surfactants in the interlayer space of clay [25-27].

In the current study, a new computation modelling calculation is introduced to demonstrate more detailed description of surfactant arrangement. The developed model will provide a better understanding of the relationship between surfactant arrangement and the adsorption behaviour of the organoclay. It will also support adsorption mechanisms for the uptake of organic pollutants from an aqueous solution. To examine adsorption capacities, p-chlorophenol (PCP) was chosen as the selected sorption test molecule and adsorption of PCP under different environmental factors such as variation of pH and temperature were investigated. The obtained results were compared with the one from the adsorption of p-nitrophenol (PNP) which was conducted under the similar experimental conditions. Although Zhou et al. [28] previously reported some adsorption studies of PNP by organo-montmorillonite, the current study led to some different outcomes which will be further discussed in the paper.

6.2 Materials and Methods

6.2.1 Materials
The pure MMT was purchased from Sigma-Aldrich as source clay Na-montmorillonite and was used without further purification. Its cation exchange capacity (CEC) is 76.4 meq/100g (according to the specification of the product). The surfactant used in this study for the preparation of organoclay was hexadecyltrimethylammonium bromide (denoted as HDTMA, C_{19}H_{42}NBr, FW: 364.46) obtained from Sigma-Aldrich and it was used without further purification.

6.2.2 Preparation of organoclay
The modification of MMT for the preparation of organoclay was performed as follows: 4 g of MMT was initially dispersed in 400 mL of deionised water with a Heidolph magnetic stirrer for about 30 min. A stoichiometric amount of the surfactant dispersed in 100 mL of deionised water was stirred for 30 min. The dissolved surfactant was slowly added to the clay suspension at room temperature.
The CEC of the MMT was 76.4 meq/100g, which represents the potential loading of the clay with the cationic surfactant. For instance, 1.0 CEC correlates with the addition of 76.4 meq of cation per 100 g of MMT intercalated into the MMT. During the synthesis, a range of surfactant loadings which would correlate with CEC values from 0.5 to 2.0 CEC was prepared and labelled as 0.5 CEC-S, 1.0 CEC-S, 1.5 CEC-S and 2.0 CEC-S. The mixtures were stirred for 3 h at room temperature using a Heidolph magnetic stirrer. All organoclays were washed free of bromide anions (as determined by AgNO₃), filtered by vacuum, dried at room temperature and dried further in an oven (at 65 °C) for 12 h. The dried organoclays were ground in an agate mortar and stored in a vacuum desiccator for a week.

6.2.3 Characterisation methods
The prepared organoclays were characterised by X-ray diffraction (XRD), surface area measurement (BET), Fourier transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS). XRD for obtaining basal spacing \(d_{(001)}\) values was operated and the method was described in the paper by Park et al. [29]. The BET specific surface area, pore structure parameters were characterised from N₂ adsorption-desorption isotherms using a Micromeritics Tristar 3000 instrument. The MMT and organoclays were pre-heated at 90 °C under N₂ over night on a Micrometrics Flowprep 060 degasser. A Nicolet Nexus 870 FT-IR spectrometer with a smart endurance single bounce diamond ATR cell was applied to collect FT-IR spectra over the spectral range of 550 – 4000 cm\(^{-1}\) with a total of 64 scans and a resolution of 4 cm\(^{-1}\). With the GRAMS (Galactic Industries Corporation, Salem, NH, USA) and the Jandel ‘Peakfit’ software package, baseline adjustment and band fitting \((R^2 > 0.99)\) for the infrared spectra was performed. To obtain XPS spectra, dried samples of MMT and the organoclays were applied to the double sided adhesive tape on a standard sample bar which was attached to the sample rod of the Load Lock system for initial evacuation to \(10^{-6}\) torr. The sample bar was transferred to the UHV sample analysis chamber (SAC) from a Kratos AXIS Ultra equipped with a monochromatic Al X-ray source at 225 W. A survey scan was undertaken for each analysis from 0 to 1200 eV with a dwell time of 100 ms, pass energy of 160 eV at step of 1eV with one sweep. High resolution analyses were run at 40 eV at intervals of 50 meV.
6.2.4 Molecular mechanical calculations

The conformational analysis of MMT intercalated with HDTMA complexes was performed by molecular mechanical calculations using the MMFF parameter set of the Spartan 02’ program (Wavefunction Inc., USA). The structure of organoclays was built up with 1024 + 2×62 atoms, taking into consideration the characteristics of the model and the required computational time. The geometry of the organoclays and the corresponding energy levels were determined by changing the basal spacing between 13 and 24 Å with equal steps of 1 Å. The position of HDTMA in the interlamellar gallery was investigated at 0.5, 1.0 and 2.0 CEC separately. The basal spacing was set and maintained at the experimental value obtained by XRD during geometry optimisation. With the molecular mechanical (MM) methods the conformational analysis of the reagents in the interlamellar space was made. Despite the obvious uncertainties concerning the energy levels, the comparison of the different structure is feasible since these uncertainties are the same for each configuration. The Lennard-Jones type energy profile is very useful for understanding the changes in system energy as a function of the interlayer distance. The quantitative determination of the energy differences as a function of the CEC load requires a detailed calculation with the density-functional theory method (DFT method).

6.2.5 Adsorption experiments

Batch experiments were carried out to test the adsorption of PNP and PCP on montmorillonite and modified clays. An initial experiment was conducted to determine the amount of adsorbent required. From the result, 0.3 g of the prepared adsorbents were dispersed in 30 mL of aqueous PNP and PCP solution (100 mg/L for the adsorption, 5 – 250 mg/L for isotherms study). The mixture was continuously agitated on a shaker for 12 h at room temperature. The initial pH of PNP and PCP was close to pH 5 – 6. After shaking, the mixture was centrifuged at 3000 rpm for 10 – 15 min and the supernatant was analysed on a UV-Vis spectrophotometer (Cary 100) at 317 nm and 279 nm for PNP and PCP, respectively. To examine the adsorption kinetics, 0.3 g of the adsorbents were added to 30 mL of 100 mg/L aqueous phenolic solution. The mixture was agitated for 10, 20, 30, 40, 50, 60, 70, 80 and 120 min and adsorption isotherms were performed at 23 and 35 ºC, respectively. Similarly, the pH of the PNP and PCP solutions was adjusted from 2 to 9 or 10 by
dropping either diluted HCl or NaOH (0.1M). The wavelength of the maximal absorption ($\lambda_{\text{max}}$) for PNP solution (pH>7) was shifted to higher wavelength at 425 – 427 nm. When PCP solution was prepared over pH 7, the peak maximum ($\lambda_{\text{max}}$) shifted to 297 – 299 nm. The quantity of the adsorbed PNP and PCP was calculated using the following equation [30].

$$q_e = \frac{V(C_i - C_e)}{MX1000}$$

where, $q_e$ is the amount of solute adsorbed on the adsorbent (mg/g), $C_i$ is the initial concentration of the solute (mg/L), $C_e$ is the equilibrium concentration of the solute (mg/L), $V$ is the volume (mL), and $M$ is the mass of the adsorbent (g).

6.3 Results and discussion

6.3.1 Characterisation of organoclays

6.3.1.1 XRD

The XRD data of pure montmorillonite and organoclays prepared at different surfactant loadings were described in the paper published by Park et al. [29] and summarised in Table 6.1. To summarise, the sodium exchanged montmorillonite has a $d$-spacing of 12.5 Å which expanded when the ions were exchanged with surfactant. Upon increasing the surfactant loading, the interlayer spacing of organoclays gradually increased. The change in structural configuration of the molecules is assigned based on the observed interlayer spacing of MMT and organoclays. There is a lateral monolayer arrangement in 0.25 CEC and 0.5 CEC. The basal spacing at 18.2 Å with a shoulder of 22.0 Å indicates a lateral bilayer arrangement and the $d$ spacing of 22.0 Å at 2.0 CEC suggests a pseudotrimolecular layer arrangement.

6.3.1.2 Surface area measurement

The structural parameters of MMT and organoclays including specific surface area ($S_{\text{BET}}$), pore volume ($V_p$), as well as average adsorption and desorption pore diameter values are summarised in Table 6.1. Figure 6.1 presents the nitrogen adsorption-desorption isotherms of MMT and the organoclays and it indicates that it conforms to a Type II in the Brunauer, Deming, Deming and Teller (BDDT) classification [31]. The large uptake of nitrogen was observed when it was close to saturation pressure and the apparent adsorption step with a sharp decline desorption branch exhibits
multilayer adsorption and implies the presence of mesopores [32-34]. This is in a good agreement with pore diameter calculated from the Barrett-Joyner-Halenda (BJH) desorption isotherm as shown in Table 6.1. According to Gregg and Sing [35], the hysteresis loops of isotherms for these materials followed H5 in the IUPAC classification and described as “ink-bottle” like pores in the clays.

Table 6.1 Structural parameters of MMT and organoclays

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a BJH desorption cumulative pore volume of pores between 1.7 and 300 nm in diameter. b Adsorption average pore diameter (4V/A by BET). c Barrett-Joyner-Halenda (BJH) desorption average pore diameter (4V/A).

Figure 6.1 Nitrogen adsorption-desorption isotherms of MMT and organoclays
The BET surface area and pore volume calculated for MMT and the organoclays in Table 6.1 shows that they decreased gradually in the order: MMT>>0.25 CEC-HDTMA>0.5 CEC-HDTMA>1.0 CEC-HDTMA>1.5 CEC-HDTMA>2.0 CEC-HDTMA. This can be explained by the observations that the packing density of organoclays increases with increasing surfactant loading in clays and the arrangement of surfactant molecules changes from being parallel to silicate surface within interlayer space to surfactant chains which are at angles to the silicate surface. Organoclays prepared at higher surfactant loadings have more sorption sites in the interlayer space and lead to increase in adsorption and desorption pore diameter and decrease in both surface area and pore volume, accordingly. These kinds of pores are like “house of cards” structure [36]. Using these two results, two different groups can be created. Group I includes organoclays prepared at low surfactant loading (e.g. 0.25 CEC-HDTMA, 0.5 CEC-HDTMA and 1.0 CEC-HDTMA), while Group II has organoclays prepared over 1.0 CEC (e.g. 1.5 CEC-HDTMA and 2.0 CEC-HDTMA). These two groups are well-resolved by the XRD patterns obtained from XRD. From this result, it appears that the loaded surfactant plays an important role in the distribution of the structure of organoclays which further determines the sorption mechanisms.

6.3.1.3 FT-IR

Understanding the molecular environment of intercalated surfactant within organoclays is important and we have used infrared spectroscopy to investigate this. There are several distinguishing regions: (i) OH stretching region (3700 – 3000 cm\(^{-1}\)), (ii) CH stretching region (2900 – 2800 cm\(^{-1}\)), (iii) HOH bending vibration region (1700–1600 cm\(^{-1}\)) and HCH bending vibration region (1520 – 1400 cm\(^{-1}\)).

6.3.1.3.1 OH stretching region

The infrared spectrum of the OH stretching region is characterised by two main bands in the 3700 – 3000 cm\(^{-1}\) range and is shown in Figure 6.2. There are two different OH stretching vibrations in this region. A sharp intense peak at 3631 cm\(^{-1}\) for MMT is assigned to OH stretching vibrations for the structural hydroxyl group, whereas the broad bands at 3402, 3330 and 3239 cm\(^{-1}\) are ascribed to hydrogen bonded water molecules adsorbed within the interlayer of the clay. The broad bands between 3500 – 3200 cm\(^{-1}\) were relatively dependent on the concentration of surfactant while the sharp hydroxyl band was relatively steady. At the low surfactant
loading of 0.25 CEC-HDTMA, the broad adsorption band was near 3365 cm\(^{-1}\) with shoulders at 3440 and 3247 cm\(^{-1}\). As the surfactant loading reaches 1.0 CEC, the broad band shifted slightly to 3360 cm\(^{-1}\) and further increased to 3383 cm\(^{-1}\) when the surfactant loading was 2.0 CEC. The change in wavenumber is closely related to the environment of the water. This indicates that water molecules in MMT are gradually displaced with the loaded surfactant in the interlayer space and the amount of water decreases. Hence, the internal surface of clays becomes more hydrophobic.

![Figure 6.2 Infrared spectra of MMT and organoclays in 3900 – 3000 cm\(^{-1}\) spectra range](image)

**Figure 6.2 Infrared spectra of MMT and organoclays in 3900 – 3000 cm\(^{-1}\) spectra range**

6.3.1.3.2 CH stretching region

The spectra of the CH stretching region for MMT and organoclays at different surfactant loadings are shown in Figure 6.3. Compared to MMT, the bands between 2700 and 2900 cm\(^{-1}\) are attributed to CH stretching vibrations from the surfactant molecules and there are antisymmetric \(v_{as}(\text{CH}_2)\) and symmetric \(v_s(\text{CH}_2)\) stretching modes observed for organoclays modified with HDTMA. Both antisymmetric and symmetric CH stretching modes of amine chains were shifted towards lower wavenumbers as the surfactant loadings increased. This shows the conformational
differences among the organoclays intercalated with HDTMA at the various CEC concentrations. In particular, the CH antisymmetric modes were significantly shifted to lower wavenumbers (from 2927 to 2918 cm$^{-1}$) upon increasing surfactant loadings. It is suggested that these CH stretching peaks are relatively sensitive to conformational changes in the chain within the interlayer and their wavenumbers decrease as the loading of surfactant increases from 0.25 CEC to 2.0 CEC. Similar results have been reported previously by Xi et al. [37]. Thus, the sensitive CH stretching bands can be qualitatively used to monitor the conformational changes of the chain. A significant wavenumber shift also indicates that more gauche conformational molecules are introduced with reduction of the alkyl chain length. The conformation of the adsorbed long alkyl surfactant progressively form solid-like molecular environment with high packing density and ordered surfactant packing, which can be characterised by XRD.

6.3.1.3.3 HOH and HCH bending vibration regions

The HOH bending region of the adsorbed water molecules is observed in the 1700 – 1600 cm$^{-1}$ range (Figure 6.4a). The Figure shows the changes of the adsorption band related to HOH bending vibrations on MMT and organoclays. The water bending modes shifted to higher wavenumbers from 1629 (with a shoulder of 1649 cm$^{-1}$) to 1645 cm$^{-1}$ with the increase of surfactant loading up to 2.0 CEC. The intensity of the peak was gradually decreased and this corresponds to the decreased amount of hydrogen bonded water molecules. This effect is due to the replacement of water by the surfactant molecules within the interlayer space of clay and with the intercalation of surfactants, the surface property of MMT tends to convert from hydrophilic to hydrophobic.

The infrared spectra of HCH bending for MMT and organoclays are shown in Figure 6.4b. Major peaks in this region are due to the methylene scissoring modes and the HCH deformation of HDTMA intercalated into MMT. The infrared spectrum of MMT was different from those of the organoclays. The bands at 1506, 1480, 1451 and 1420 cm$^{-1}$ were observed for MMT but the two bands at 1506 and 1420 cm$^{-1}$ were no longer observed in the organoclays intercalated with HDTMA. The three small peaks at 1488, 1474 and 1465 cm$^{-1}$ shown at 0.25 CEC reflected the increase in surfactant loading.
Figure 6.3 Infrared spectra of MMT and organoclays in 2900 – 2800 cm⁻¹ spectra range

Figure 6.4 Infrared spectra of MMT and organoclays in 1720 – 1560 cm⁻¹ spectra range (a) and 1560 – 1400 cm⁻¹ spectral range (b)
6.3.1.4 XPS

XPS technique was applied to probe the surface chemical composition of the organoclays, and the XPS survey scans are presented in Figure 6.5. The survey scans showed that the chemical compositions of the organoclays are similar to those of the organoclays reported in our previous study [33, 38]. Trace amounts of iron and magnesium, located in the structure of MMT rather than in the interlayer space, were detected and the observed nitrogen and carbon peaks are from the organic surfactant.

Figure 6.5 Examples of XPS survey scan spectra (1.0 CEC and 2.0 CEC-HDTMA)
Figure 6.6 XPS high resolution spectra of Si 2p and Al 2p for organoclays at 1.0 CEC and 2.0 CEC
Highly distinct peaks of silicon and carbon were seen and the ratio of C/Si increased with increasing surfactant loadings: 1.95 (0.5 CEC-HDTMA) < 2.05 (1.0 CEC-HDTMA) < 2.38 (1.5 CEC-HDTMA) < 3.35 (2.0 CEC-HDTMA). The binding energy obtained from the high resolution XPS supported the changes in the structure. Thus, the reduced binding energy of Si 2p and Al 2p observed from the high resolution spectra in Figure 6.6 indicates changes in the structures of organoclays intercalated with surfactant molecules. The change in binding energy is also shown between C 1s within organoclays (summarised in Table 6.2).

Unlike the decreasing binding energy observed in the Si and Al spectra, two peaks of C 1s are assigned to C-C and C-N bond at 281 and 283 eV, respectively. It is evident from the summarised binding energy of C 1s in Table 2 that the binding energy of C-C bond gradually increased upon increasing the surfactant loading while that of C-N bond was independent of the surfactant loading. Although changes in surfactant arrangement and packing density within organoclays occurred as a result of increased surfactant loadings, the bonding between the nitrogen group of the surfactant and the negatively charged clay surface is relatively sustained. A molecular mechanical model of the structural change within the organoclays was obtained to support the conformational changes in surfactant molecules within organoclays determined by XPS techniques.

Table 6.2 Binding energy and atomic contents of C 1S for the organoclays

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6.3.2 Molecular mechanical modelling

The conformational change in the surfactants was examined using molecular mechanical calculations. The energy profile of the organoclay compounds is presented in Figure 6.7. The basal spacing increased with the cation exchange capacity (CEC) and the forces holding the complex together showed a local
minimum (inflection point) at basal spacing over 17 – 18 Å. With a basal spacing of 21 – 22 Å for the TOT-HDTMA-TOT complex the TOT-TOT layers still influenced each other. However, when the basal spacing was further expanded above this point, the TOT layers were hardly able to detect each other due to the increased distance. Thus, only the interactions of the TOT-HDTMA system can be investigated in this study. From the energy profiles shown, there are two possibilities to delaminate the MMT into single TOT layers: (i) at CEC = 1.0, the HDTMA cation is changed to another cation which is big enough to increase the basal spacing to at least 21 Å rather than being washed out with a polyelectrolyte; (ii) the amount of HDTMA is increased to CEC ≈ 2.0 in the interlamellar space and then washed out with a polyelectrolyte.

Figure 6.7 Energy profile of MMT-HDTMA complexes as a function of basal spacing
Figure 6.8 The geometry of HDTMA cations in the interlayer space
The arrangement of surfactant in the interlayer space of MMT was also investigated (see Figure 6.8). As shown in Figure 6.8, the HDTMA cation was present as a monolayer with a head-to-tail position up to CEC $\approx 0.5$ (14 – 15 Å of basal spacing). Upon increasing the surfactant loading, the reagent took up an alternating-type of pattern. When CEC reached 1.0, the basal spacing of the reagent increased continuously and a double-layer pattern was reached between 16 to 18 Å. The final position of the reagent was determined by the constant negative charge of the TOT layer surface and the highly polarized nature of the rod-like molecule. As the CEC value increased, the corresponding increase in the basal distance and the space available allows alternating positions for the reagent. Thus, the initial 180° angle corresponding to the head-to-tail-to-head pattern gradually decreased to a value where the attracting and repulsive forces between the HDTMA molecules are in equilibrium. The computational model shows that the energy levels of the basal distances and the corresponding geometry of the surfactant at minimum or local minimum are well approximated. It also showed that the basal distance where the TOT layers are no longer in interaction can also be determined. In addition, the study indicates that the arrangement of surfactant is significantly influenced by the surfactant loading. The proposed conformational change of surfactant molecules enhances the visual understanding of the results obtained from characterisation methods such as the XRD and surface analysis of the organoclays.

6.3.3 Adsorption experiments

6.3.3.1 Effect of surfactant loading
Based on the characteristics of MMT and the modified clays, the adsorption capacity of the organoclays was investigated for the uptakes of PNP and PCP from aqueous solutions. After 12 hr agitation time, the maximum percentages of adsorbed PNP and PCP by the organoclays is presented in Figure 6.9.
Figure 6.9 Percentage of PNP and PCP removed by the organoclays

It was found that the amount of phenolic compounds removed by the unmodified MMT is negligible (not shown in Fig. 6.9). This suggests that the modified clays are better adsorbents for the removal of PNP and PCP from water. When the surfactant molecules were increased, the amount of adsorbed PNP and PCP also gradually increased. The obtained results are in good agreement with the molecular calculation model; the larger interlayer space within organoclays provides a higher potential for the uptake of more phenol pollutants. In particular, at 1.5 CEC the organoclays removed 98.2 % of PNP and 86 % of PCP, respectively (100 mgL$^{-1}$, 23 ºC). The adsorbed amount of PCP and PNP is similar as the surfactant loading increases up to 2.0 CEC. It can be concluded from the current study that the adsorption capacity of the organoclays is close to 100 % for PNP and the organoclays are more efficient in adsorbing PNP than PCP from water. The phase for the uptakes of phenolic compounds is critical for an efficient adsorbent in the environment and the kinetic study for the removal of the PNP and PCP by the organoclays was conducted.

6.3.3.2 Kinetic study

The main objective of this section of the study is to examine the relation between agitation time and the amount of adsorbed PNP and PCP on organoclays as described in Figures 6.10 and 6.11. The amount of adsorbed PNP appears to be proportional to
the agitation time. The initial amount of adsorbed PNP increased rapidly up to 50 min. Later adsorption of PNP occurred slowly and the maximum of adsorbed PNP is reached around 60 min. The removal of PCP occurred in a similar way. However, the PCP was more rapidly adsorbed within 40 minutes and slowly reached the maximum amount within 80 min.

There are several simplified kinetic models such as pseudo-first order equation, pseudo-second order equation, and intra-particle diffusion model. Of these, the pseudo-first order rate, which is expressed by Lagergren [28, 39, 40] is the most widely used for the sorption of liquid/solid system based on solid capacity. The rate equation is expressed in the form:

$$\frac{dq_t}{dt} = k_1(q_{e1} - q_t)$$

where, $k_1$ is the rate constant of pseudo-first order adsorption (min$^{-1}$), $q_{e1}$ is the amount of solute adsorbed at equilibrium (mg/g) and $q_t$ is the amount of solute adsorbed at any time $t$ (mg/g).

By integrating this equation for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$. Eq. (6 – 1) can be expressed as:

$$\ln(q_e - q_t) = \ln q_{e1} - k_1t$$

A pseudo-second order rate expression based on the sorption capacity is proportional to the number of active sites occupied on the sorbent and its equation can be written as:

$$\frac{dq_t}{dt} = k_2(q_{e2} - q_t)^2$$

where, $k_2$ is the rate constant for pseudo-second order adsorption (g/mg·min), $q_{e2}$ is the amount of solute adsorbed at equilibrium (mg/g) and $q_t$ is the amount of solute adsorbed at any time $t$ (mg/g). By integrating Eq. (6 – 3) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$. Eq (6 – 4) is obtained:

$$\frac{t}{q_t} = \frac{1}{(k_2q_{e2}^2)} + \frac{t}{q_{e2}}$$
Figure 6.10 Effect of adsorption time on the removal of PNP by organoclays (100mg/L of PNP)

Figure 6.11 Effect of adsorption time on the removal of PCP by organoclays (100mg/L of PNP)
The constants can be determined from the linear plot $t/q_t$ against $t$ (shown in Figure 6.12).

The model of intra-particle diffusion was suggested by Weber and Morris [41]. This model is frequently used to describe the rate determining step of the sorption process occurring on porous adsorbents which is theoretically calculated using the equation shown below.

$$q_t = K_{\text{diff}} \sqrt{t} \quad \text{Equation 6 – 5}$$

where $K_{\text{diff}}$ is the rate constant for intra-particle diffusion (mg/g·min$^{1/2}$).

The rate constant $K_{\text{diff}}$ can be calculated from the plots of $q_t$ versus $t^{1/2}$ and Weber and Morris found that the uptake of the solute is proportional to $t^{1/2}$ rather than $t$. Due to the limitation of pseudo-first and -second order models to provide the diffusion mechanism, this model was applied in this study. If the plot is linear, then intra-particle diffusion is involved in the adsorption process and it is the controlling step if the line passes through the origin. From Figure 6.13, several steps were observed including an initial curve, linear relationship, and lastly, a plateau. According to previous studies [42-44], the initial curve can be assigned to the bulk diffusion and the linear process to the intra-particle diffusion. However, none of them pass through the origin. Hence, intra-particle diffusion is involved but it is not a controlling step during the adsorption processes.

The parameters of pseudo-first, -second, and intra-particle diffusion model were obtained and summarised in Table 6.3. It is evident from the Table that the rate constants of intra-particle diffusion on organoclays were higher for PCP than PNP. The pseudo-second order kinetic model fitted better than the pseudo-first order model in this study which is similar to the result reported by Zhou et al. [28].
Figure 6.12 Test of the pseudo-second equation for the sorption of PNP (a) and PCP (b)
This model is also well fitted in the previous studies [45]. This indicates that organoclays reached equilibrium in the order: 0.5 CEC-HDTMA > 1.0 CEC-HDTMA > 1.5 CEC-HDTMA ≈ 2.0 CEC-HDTMA. It also means that organoclays prepared at lower surfactant loadings tend to reach equilibrium quicker than those at higher surfactant loadings. This is in agreement with the change of pore size obtained from BET (see Table 6.1). The loaded surfactant molecules block the pores and the sizes of pores become smaller. Hence, the adsorption of PNP and PCP onto the organoclays slows down. It also suggests that this sorption system fits the pseudo-second model based on the assumption that the rate-limiting step may be chemical sorption or chemisorptions and the model provides the best correlation of the experimental data [39]. Therefore, the chemical reaction in this study significantly controls the rate controlling step.

### Table 6.3 Model parameters for adsorption of the PNP and PCP on the organoclays

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</table>
Figure 6.13 Intra-particle diffusion for the adsorption of PNP (a) and PCP (b)
6.3.3.3 Effect of pH

Most phenols are present as weak acids in aqueous solutions and the dissociation of the solutes and their derivative molecules are strongly dependent on pH. This study investigates how the adsorption of phenolic compounds is influenced at varied pH environments and the optimum pH condition was determined in the adsorption of the phenolic compounds. The pH of the solution ranged from 2 to 9 or 10 and the initial concentration of PNP and PCP solution was 100 mg/L. The uptake of PNP and PCP by organoclays at different pH is presented in Figures 6.14 and 6.15.

It is observed from the Figures 6.14 – 6.15 that the PNP adsorption on organoclays increased when the value of pH increased from 2 to 3. The maximum adsorption was maintained until the pH of 5 is reached. However, it is recognised that the adsorption of PNP decreased significantly when pH value rose beyond 6. On the other hand, the decrease in the uptake of PCP occurred when the pH value is greater than 8. These changes in adsorption can be explained by the surface charge of clays and dissociation behaviour of the phenolic compounds [30]. In the structure of the MMT, Si-O bond (in the tetrahedral sheets) on the external surface of clay is weaker and becomes SiO$^-$ and further converts to Si-OH by accepting protons or hydroxyls. The change of surface charge is caused by the presence of surface hydroxyl groups such as SiOH, which is subject to protonation or deprotonation, depending on the pH variation.

As the pH of the solution increases, the surface functional groups are partially or fully deprotonated. Therefore, loss of positive charge on the surface and increase of negative charge occurred. Both phenolic compounds are weak acids with dissociation constant (pKa) of 7.15 and 9.18, respectively [46]. They exist in their neutral forms at low pH or pH < pKa and prevail anionic species when the solution pH > pKa. This indicates that decreasing pH increases the sorption capacity of the organoclays due to the formation of PNP and PCP, which have great affinities for the interlayer organic phase of the organoclays. In addition, the neutral PNP and PCP compounds are more adsorbed onto organoclays than the anionic, because the organic phase acts as an efficient partition medium for the uptake of neutral PNP and PCP at low pH levels or acidic conditions [47]. Thus, higher sorption of phenolic compounds was measured on 1.5 and 2.0 CEC organoclays compared to the 0.5 and 1.0 CEC ones, most likely due to the better partition medium provided by the high basal spacing.
Figure 6.14 Effect of final pH on the adsorption of PNP (pH_{in} = 5, C_{in} = 100 mg/L)

Figure 6.15 Effect of final pH on the adsorption of PCP (pH_{in} = 5, C_{in} = 100 mg/L)
For the alkaline solutions, the increased negative charge on the clay surface and anionic species of PNP and PCP electrostatically repel each other, leading to decrease in adsorption. It is interesting to notice that organoclays prepared at 2.0 CEC adsorbed larger amounts of the phenolic compounds compared with the other organoclays over the entire pH range studied. The produced result followed a similar trend with the previous studies by Sarkar et al. [30], Kim et al. [48] and Gupta et al. [49, 50]. In the paper by Zhou el al. [28], a different adsorption pattern was observed for PNP and the variation in the results for the two studies may be due to the different experimental environments and conditions used.

6.3.3.4 Mechanism of adsorption of the phenolic compounds onto organoclays

6.3.3.4.1 Adsorption model theory

It is necessary to understand the adsorption isotherm for the mechanism of adsorption system in the study. Certain parameters obtained from the equilibrium equation indicate the surface properties of the sorbent and its adsorption capacity, leading to the prediction of the maximum equilibrium adsorption. It is possible to apply several adsorption isotherm models and Langmuir and Freundlich adsorption models are widely used in many studies [8, 51, 52]. In this present study, Langmuir and Freundlich adsorption isotherms were applied to investigate the sorption mechanisms of phenolic compounds.

6.3.3.4.1.1 Langmuir isotherm

The theory of Langmuir isotherm was proposed by Langmuir [53] and it described the relation between the adsorption of adsorbate and the surface of the adsorbent. The adsorbate is strongly attracted to the surface and it is assumed that a monolayer adsorption is involved. The surface has specific homogenous sites and all the vacant sites are equally sized and shaped. Once adsorption takes place at specific sites within the adsorbent and no further adsorption occurs at the specific sites. Hence, the adsorption to the surface is strongly related to the driving force and surface area. The Langmuir model can be expressed as equation in the form:

\[ q_e = \frac{x}{M} = \frac{K_L C_e}{1 + b_L C_e} \]

Equation 6 – 6
where, \( q_e \) is the amount of adsorbate adsorbed at equilibrium (mg/g), \( x \) is the equilibrium concentration of the adsorbate in solid phase (mg/L), \( M \) is mass of adsorbent in the free volume (mg/L), \( K_L \) is Langmuir constant related to saturated monolayer (L/mg), \( b_L \) is Langmuir isotherm constant related to energy or net enthalpy, \( C_e \) is the equilibrium concentration of the adsorbate remaining in solution (mg/L). Equation (6) can be rewritten in the linear form:

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}
\]

Equation 6 – 7

where, \( q_m \) is the maximum adsorption capacity of the adsorbate (mg/g).

A linear plot of \( C_e/q_e \) versus \( C_e \) is obtained and the constants \( q_m \) and \( K_L \) can be calculated. To predict the favourable or unfavourable adsorption process, a dimension constant, \( R_L \) is also calculated by the following equation [54].

\[
R_L = \frac{1}{1 + K_L C_0}
\]

Equation 6 – 8

where, \( K_L \) is the Langmuir constant and \( C_0 \) is the initial liquid phase concentration (mg/L). The adsorption process is considered as unfavourable (when \( R_L > 1 \)), linear (when \( R_L = 1 \)), favourable (when \( 0 < R_L < 1 \)), and irreversible (when \( R_L = 0 \)).

6.3.3.4.1.2 Freundlich isotherm

Freundlich suggested an empirical expression to describe the adsorption theory [55]. The model is based on the assumption that the adsorbent surface is heterogeneous and consists of different classes of adsorption sites. The adsorption takes place at the heterogeneous surfaces or surfaces supporting sites of varied affinities [56]. This model is only capable of predicting the infinite surface coverage which involves the multilayer adsorption of the surface [57]. The Freundlich isotherm is shown below:

\[
q_e = K_F C_e^{1/n}
\]

Equation 6 – 9

where, \( q_e \) is the amount of adsorbed solute, \( K_F \) is Freundlich constant related to the adsorption capacity (L/mg), \( n \) is Freundlich constant related to the adsorption
intensity of the adsorbent, and $C_e$ is the concentration of solute in the solution at equilibrium (mg/L).

The linear form of the Freundlich isotherm can be represented as equation (10):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Equation 6 – 10

The Freundlich constants $K_F$ and $n$ can be determined from a linear plot of $\ln(q_e)$ versus $\ln(C_e)$. When the value of $n$ is higher than 1 ($n > 1$), the adsorption process is favourable over the entire range of concentration and multilayer sorption is formed on the surface of the adsorbent. The adsorption process is more favourable at high concentrations than at low concentrations when the value of $n$ is less than 1 ($n < 1$).

### 6.3.3.4.2 Adsorption of the phenolic compounds

Based on the above models, the mechanisms for the uptake of PNP and PCP on the organoclays are modelled. The equilibrium parameters were determined and summarised in Table 6.4.

As shown in the Tables 6.4, $R^2$ values obtained for Freundlich isotherm model are generally higher than those obtained by the Langmuir model. Therefore, the equilibrium data for both PNP and PCP were better fitted into the Freundlich isotherm model than the Langmuir model. This suggests that the adsorption process of these phenolic compounds onto organoclays is controlled by several mechanisms. The Freundlich parameters $n$ and $K_F$ provide substantial information to measure the strength of adsorption for phenolic compounds and the values are listed in Table 6.4. The Freundlich affinity index, $n$ values, measures the adsorption strength of the phenolic compounds and the values for PNP were larger than those for PCP. The value of $n$ ($n > 1$) obtained for PNP indicates the adsorption of PNP is favourable over the entire range of concentrations used in this current study. On the other hand, the adsorption system is better at higher concentrations of PCP solutes based on the lower value of $n$ ($n < 1$).

The value of the binding affinity constant, $K_F$, becomes larger as the surfactant loading increases. This shows that the adsorption capacity of organoclays intercalated at higher surfactant loadings are better for the uptakes of the phenolic compounds.
Table 6.4 Langmuir and Freundlich isotherm constant and values of parameters for adsorption of PNP and PCP on the organoclays at 23 and 35 ºC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir equation</th>
<th>$q_m$ (mg g$^{-1}$)</th>
<th>$K_L$ (L mg$^{-1}$)</th>
<th>$R^2$</th>
<th>$R_L$</th>
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<th>$q_m$ (mg g$^{-1}$)</th>
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<th>$R^2$</th>
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<th>Sample</th>
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<th>$K_F$ (L mg$^{-1}$)</th>
<th>$n$</th>
<th>$R^2$</th>
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Several mechanisms of adsorption have been postulated such as electrostatic interaction, donor-acceptor complex formation, hydrophobic interaction and hydrogen bonding. The loaded surfactants with CEC less than 1.0 tend to enter the interlayer space of the clays and the formed organic micelles contribute an organic medium for the interaction of the phenolic compounds. At the same time, adsorption occurs through electrostatic interaction between phenolic anions and intercalated surfactant cations. Once the surfactants exceed 1.0 CEC (1.5 and 2.0 CEC-HDTMA), the interlayer space of clays is filled by loaded surfactants which form a partition medium that results in the strong adsorption affinity to organic pollutants via hydrophobic interaction. Hence, the adsorption system of these phenolic compounds onto organoclays is likely to involve multilayer sorption, mainly partitioning process rather than surface interaction. The organoclays have a greater capacity for the adsorption of PNP rather than PCP in the aqueous solutions. This may be due to the stronger hydrophobicity of PNP over PCP. A similar result was also reported by Akcay and akcay [46]. In the adsorption process of PNP, the formation of donor-acceptor complex is involved so that the modified clays, including metal cations create Lewis acid sites which are coordinated with the phenolic compounds that act as Lewis bases in the aqueous solution. Due to the high affinity of PNP for organoclays, higher sorption energy is expected for PNP than for PCP and the relatively decreased K_F values with increased temperature from 23 to 35 °C are responsible for the exothermic reaction observed during this adsorption process.

6.4 Conclusions
In this study, montmorillonite was converted to hydrophobic organoclays by intercalation with cationic surfactants in order to improve its adsorption capacity for organic pollutants. The synthesised organoclays were characterised using various techniques. As the surfactant loading increases, structural changes of HDTMA molecules occur, leading to expanded basal spacings. The conformational changes of the surfactant molecules within the interlayer space were confirmed by computational molecular models. The characterised organoclays were tested for their abilities to remove PNP and PCP from aqueous solutions and the experiments showed that the organoclays are more effective in removing PNP than PCP. In particular, the organoclays intercalated with higher surfactant loadings afford better
uptakes of the phenolic compounds. However, as the loaded surfactant blocks the pores of the clays, the process of reaching the equilibrium is slowed down. The process was best explained by involving pseudo-second order model and intra-particle diffusion, which was not the controlling step. For the adsorption of phenolic compounds by organoclays, Freundlich isotherm gave the best fit and this indicated that the adsorption system is likely to involve multilayer sorption. It is noted the loaded surfactant molecules in the interlayer space act as a partition phase to strongly attract to the organic pollutants via hydrophobic interaction. Therefore, the prepared organoclays are more efficient adsorbents for the removal of PNP than of PCP due to differences in their hydrophobicity properties as reflected by the strong adsorption mechanism of partitioning affinities observed in this study. This study demonstrated the adsorption of the phenolic compounds onto organoclays, thus promoting the potential utility of the organoclays as adsorbents for environmental pollutants.

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6.5 References


This paper was originally published:

PREFACE
The previous paper confirmed the conformational changes of HDTMA cations in the interlayer space of clays by the MM calculation. The fully characterised organoclays were tested for their abilities to remove $p$-nitrophenol (PNP) and $p$-chlorophenol (PCP). The investigation showed that the organoclays afforded better uptakes of the phenolic compounds at higher surfactant loadings. It was noted that the organoclays were more effective for the removal of PNP than PCP and this was likely due to the different hydrophobicities of the obtained organoclays.

The following chapter established similar adsorption capabilities for the removal of PNP and PCP by organoclays intercalated with DDTMA and DDDMA. Additionally, MM calculation was also employed to demonstrate the arrangement of DDTMA and DDDMA cations in the interlayer space. The obtained adsorption capacities of two different types of organoclays were compared. By in-depth investigations under different experimental conditions, the conditions for optimum sorption of the phenolic compounds and possible mechanisms were determined.
STATEMENT OF CONTRIBUTION OF CO-AUTHORS

The authors listed below have certified* that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and
5. they agree to the use of the publication in the student's thesis and its publication on the QUT ePrints database consistent with any limitations set by publisher requirements.

In the case of this chapter:

Adsorption of phenolic compounds by organoclays: Implications for organic pollutants from aqueous media, *Journal of Colloid and Interface Science* 406 (2013) 196-208

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<tr>
<td>Yuri Park (candidate)</td>
<td>Developed experimental design, conducted experiments, analysed data, and wrote the manuscript.</td>
</tr>
<tr>
<td>Godwin A. Ayoko* (Principal Supervisor)</td>
<td>Assisted in the experimental design, supervised and provided scientific advice, and edited the manuscript.</td>
</tr>
<tr>
<td>Róbert Kurdi</td>
<td>Developed computational modelling, interpreted data, and aided in presentation of the computational modelling data</td>
</tr>
<tr>
<td>Erzsébet Horváth</td>
<td>Developed computational modelling, interpreted data, and aided in presentation of the computational modelling data</td>
</tr>
<tr>
<td>Janos Kristof</td>
<td>Developed computational modelling, interpreted data, and manuscript editing</td>
</tr>
<tr>
<td>Ray L. Frost (Associate Supervisor)</td>
<td>Assisted in the experimental design, supervised and provided scientific advice, and edited the manuscript</td>
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</table>

Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

[Signature]

Name  Signature  Date

14/10/2013

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7.1 Introduction
Phenol and phenolic derivatives are released from many industries such as pharmaceutical, petroleum and petrochemical, pesticides, plastic, paper and other manufactures [1, 2]. Thus, they are considered as common environmental contaminants. The total production of phenols reached 7.8 million tons in 2001 [3] and phenolic compounds such as p-nitrophenol (PNP) and p-chlorophenol (PCP) impact unpleasant odours and tastes to drinking water and are harmful to humans and living organisms [4]. Their presence even at low concentrations can be obstacles to the acceptance of recycled water by the community. Due to their toxicity and adverse effects on the environment, phenolic compounds are listed as priority pollutants by the United States Environmental Protection Agency (EPA) [5, 6]. Their removal from industrial effluents is therefore one of challenges facing the world today and several treatment methods including biological, chemical, and physical processes are being applied before phenols are discharged into the environment [7]. While these methods are useful for removing phenols, some of them, especially secondary biological treatments are limited to the remediation of wastewater containing higher concentrations of phenolic compounds [7]. Hence, many studies have investigated the development of promising materials for the uptake of phenols at lower concentrations. In this regard, one of the widely used adsorbents is activated carbon, which has a high surface area and high adsorption capacity towards organic molecules from water [8-11]. However, activated carbon becomes ineffective for removing larger molecules (e.g. humic acid) and wastewaters containing emulsified oil and grease [12]. It is also a well-known fact that its widespread use is limited due to their high cost; hence, the search for lower-cost, economically feasible and locally available adsorbents with high adsorption capacity for the adsorption of phenolic compounds are required, such as modified montmorillonite.

Naturally abundant clay minerals have received a lot of attention as potential adsorbents due to their cost effectiveness, environmentally stability, high adsorption and ion exchange properties [13]. The commonly used clay is montmorillonite (MMT) which has a high cation exchange capacity (CEC), swelling properties, and high surface areas but it is hydrophilic. However, its hydrophilic properties can be converted to hydrophobic properties when the inorganic cations (Na$^+$ or Ca$^{2+}$) in its interlayer space are replaced with organic cations such as quaternary ammonium
cations (QACs). The resulting organoclays have been widely used as adsorbents for organic pollutants and airborne organic pollutants [3, 7, 14-18]. Previous studies [17, 19, 20] suggested that the mechanisms of the adsorption of organic pollutants are associated with the structure of QACs in the clays, including the length of the alkyl chain, packing density as well as the charge density of the clay layer.

In this study, structural changes of the unmodified MMT and organoclays are investigated and the conformational changes of surfactant molecules intercalated in the interlayer space are demonstrated using a computational modelling calculation. The obtained models will provide a better understanding of the arrangement of surfactants, which relates to the adsorption behaviour of the organoclays in terms of demonstrating the potential for the uptake of organic pollutants such as p-chlorophenol (PCP) and p-nitrophenol (PNP). This study also aims to investigate the adsorption capacity and adsorption mechanism of the organoclays prepared using different types of surfactants (mono- and di- alkyl chain). In this respect, the adsorption of PCP and PNP was conducted at different conditions such as pH and temperature, and the obtained results provided new insights into the structural properties of organoclays as well as their implications for the removal of industrial pollutants from aqueous solutions.

7.2 Experimental methods

7.2.1 Materials

The pure Na-montmorillonite (subsequently referred as MMT) was purchased from Sigma-Aldrich and was used without further purification. According to the product specification, its cation exchange capacity (CEC) is 76.4 meq/100g. Two types of cationic surfactants: (i) dodecyltrimethylammonium bromide (denoted as DDTMA, C_{15}H_{34}NBr, FW:308.34) and (ii) didodecyldimethylammonium bromide (denoted as DDDMA, C_{26}H_{56}NBr, FW:462.65), which are examples of mono- and di- alkyl chain surfactants, respectively were purchased from Sigma-Aldrich and used without further purification for the preparation of the organoclays.

7.2.2 Synthesis of organoclays

The organoclays were prepared using the same procedures as in the previous paper [21]: 4 g of MMT was initially dispersed in 400 mL of deionised water with a Heidolph magnetic stirrer for about 30 min. A stoichiometric amount of the
surfactant dispersed in 100 mL of deionised water was stirred for 30 min. The dissolved surfactant was slowly added into the clay suspension at room temperature. The CEC of the MMT was 76.4 meq/100g, which represents the potential loading of the clay with the cationic surfactant. Thus, 1.0 CEC correlates with the addition of 76.4 meq of cation per 100 g of MMT intercalated into the MMT. During the synthesis, a range of surfactant loadings which would correlate with CEC values ranging from 0.5 to 2.0 CEC were prepared and labelled as 0.5 CEC-DDTMA – 2.0 CEC-DDTMA or 0.5 CEC-DDDMA – 2.0 CEC-DDDMA. The mixture was stirred for 3 hr at room temperature using a Heidolph magnetic stirrer. All organoclays were washed free from bromide anions as determined by AgNO₃, filtered by vacuum, dried at room temperature and dried further in an oven at 60 – 65 ºC over night. The dried organoclays were ground in an agate mortar and stored in a vacuum desiccator for a week.

7.2.3 Characterisation methods
To characterise the prepared organoclays, different characterisation methods such as X-ray diffraction (XRD), surface area analysis (Brunauer, Emmett & Teller, BET method), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FT-IR) were applied. XRD was used to determine the basal spacing \( d_{(001)} \) values as described in the paper by Park et al. [22]. The XRD pattern of the organoclays intercalated with DDDMA surfactant was obtained at a low angle section between 2° and 8° (2θ) at a step size of 0.0167° with variable divergence slit and 0.25° anti-scatters. Using a Micromeritics Tristar 3000 instrument, \( N_2 \) adsorption-desorption isotherms were performed to measure the BET specific surface area and pore structure parameters. Before the measurement, the MMT and organoclays were pre-heated at 90 ºC under \( N_2 \) over night on a Micrometrics Flowprep 060 degasser. For the FT-IR, Nicolet Nexus 870 FT-IR spectrometer with a smart single bounce diamond ATR cell was applied over the spectral range of 550 – 4000 cm\(^{-1}\) with a total of 64 scans and a resolution of 4 cm\(^{-1}\). To obtain XPS spectra, dried MMT and the organoclays were applied to the double sided adhesive tape on a standard sample bar which was attached to the sample rod of the Load Lock system for initial evacuation to \( 10^{-6} \) torr. The sample bar was transferred to the UHV sample analysis chamber (SAC) from a Kratos AXIS Ultra equipped with a monochromatic Al X-ray source at 225 W. A survey scan was undertaken for each
analysis from 0 to 1200 eV with a dwell time of 100 ms, pass energy of 160 eV at step of 1 eV with one sweep. High resolution analyses were run at 40 eV at intervals of 50 meV and high resolution spectra were charge compensated by the binding energy of the C 1s peak at 284.6 eV while the peak areas and obtained high resolution spectra were fitted using CasaXPS (Casa Software Ltd., Cheshire, UK).

7.2.4 Molecular mechanical calculations
A similar procedure and condition as the previous study was applied in order to obtain the structural conformation of organoclays by the molecular mechanical calculations (MM calculations) using the MMFF parameter set of the Spartan 10’ program (Wavefunction Inc. USA) [21]. The structure of the organoclays was built up with 920 + 2×50 (for DDTMA) and 920 + 2×83 (for DDDMA) atoms based on the characteristics of the model and the required computation time. The geometry and the corresponding energy levels were determined within the basal spacing between 14 and 21 Å with equal steps of 1 Å and between 12 and 25 Å with equal steps of 1 Å for the organoclays intercalated with DDTMA and DDDMA, respectively. The experimental data of the basal spacing from XRD was set and maintained in order to obtain geometry optimisation. The position of DDTMA in the interlamellar gallery was investigated at 0.5, 1.0 and 1.5 CEC, while that of DDDMA was studied at 0.25, 1.0, 1.5 and 2.0 CEC.

7.2.5 Adsorption experiments
Batch experiments were performed to investigate the adsorption capacities of MMT and modified clays for the removal of phenolic compounds from aqueous solutions. For the initial experiments, 0.2 g of the prepared adsorbents were dispersed in 30 mL of aqueous PCP and PNP solution (100 mg/L for the adsorption, 5 – 250 mg/L for isotherm study). The mixture was continuously agitated on a shaker for 12 hr at room temperature. The initial pH of PCP and PNP was close to pH 5 – 6. After shaking, the mixture was centrifuged at 3000 rpm for 10 – 15 min and the supernatants were analysed on a UV-Vis spectrophotometer (Cary 100, Agilent Technologies) at 317 nm and 279 nm for PNP and PCP, respectively.

To undertake the adsorption kinetics, 0.2 g of the adsorbents were added to 30 mL of 100 mg/L aqueous phenolic solution. The mixture was agitated for 10, 20, 40, 60, 80, 120 and/or 180 min and adsorption isotherms were performed at 23 and 35 ºC,
respectively. Similarly, the pH of the PNP and PCP solutions were adjusted from 2 to 8 or 9 by dropping either diluted HCl or NaOH (0.1 M). The wavelength of the maximum absorption ($\lambda_{\text{max}}$) for PNP solution (pH > 7) was shifted to higher wavelength at 425 – 427 nm. When PCP solution was prepared above pH 7, the peak maximum ($\lambda_{\text{max}}$) shifted to 297 – 299 nm. The final pH of the solution was measured and it was noted that the pH changes during the adsorption were negligible.

The quantity of the adsorbed PNP and PCP was calculated using the following equation.

$$ q_e = \frac{V(C_i - C_e)}{M \times 1000} $$

where, $q_e$ is the amount of solute adsorbed on the adsorbent (mg/g), $C_i$ is the initial concentration of the solute (mg/L), $C_e$ is the equilibrium concentration of the solute (mg/L), $V$ is the volume (mL), and $M$ is the mass of the adsorbent (g).

### 7.3 Results and discussion

#### 7.3.1 Characterisation of organoclays

##### 7.3.1.1 XRD

The full XRD data for pure MMT and the organoclays prepared at different surfactant loadings were described in the paper published by Park et al. [22]. An intense $d_{(001)}$ peak at lower angles was further obtained for organoclays intercalated with DDDMA as presented in Figure 7.1.

The sodium exchanged MMT has a $d$-spacing of 1.25 nm, which expanded when ion exchange occurred with surfactant molecules. Upon increasing the DDDMA surfactant loading up to 1.0 CEC, an intense $d_{(001)}$ peak is observed at 2.69 nm with a shoulder at 1.87 nm, which represents as a paraffin-type monolayer arrangement with a lateral bilayer. As the loading of the surfactant increased above 1.0 CEC, an intense peak at 3.11 nm (with a shoulder at 2.15 and 1.52 nm) and 3.17 nm (with a shoulder at 1.72 and 1.51 nm) is formed at 1.5 CEC and 2.0 CEC, respectively. This indicates that paraffin-type bilayer arrangement with lateral mono and bilayer arrangement and/or pseudotrimolecular structure is observed. In summary, the interlayer space of the organoclays gradually increased with an increase in the surfactant loading with
concomitant changes in structural arrangement of the surfactant molecules. There is a monolayer at lower surfactant loading (0.25 and 0.5 CEC) and a lateral bilayer arrangement at higher surfactant loading (1.0 – 2.0 CEC) in the XRD pattern of the organoclays intercalated with DDTMA, whereas a lateral monolayer and bilayer arrangement is formed at lower surfactant loading (0.25 and 0.5 CEC) for the organoclays intercalated with DDDMA. A paraffin-type structure is only present when the loading of the di-alkyl chain cationic surfactant, DDDMA, is ≥ 1.0 CEC.

Figure 7.1 XRD pattern of MMT intercalated with DDDMA at lower angles

7.3.1.2 Specific surface area measurement

Nitrogen adsorption-sorption isotherms were performed to provide the structural parameters of MMT and organoclays including specific surface area ($S_{BET}$), pore volume ($V_P$), and average adsorption and desorption pore diameters which are summarised in Table 7.1. The isotherms (presented in Figure 7.2) follow a Type II in the Brunauer, Deming, Deming and Teller (BDDT) classification [23]. This indicates multilayer adsorption and the presence of mesopores based on the observation that
the large uptake of nitrogen was close to the saturation pressure and the apparent adsorption step with a sharp decline desorption branch.

![Figure 7.2 N\textsubscript{2} adsorption-desorption isotherms of MMT and organoclays](image)

**Table 7.1 Structural parameters of MMT and organoclays**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>(d_{001}/\text{nm})</th>
<th>(SL^a)</th>
<th>(S_{\text{BET}}/\text{m}^2\cdot\text{g}^{-1})</th>
<th>(V_p^b/\text{cm}^3\cdot\text{g}^{-1})</th>
<th>Mean/nm</th>
<th>BET(^c)</th>
<th>BJH(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMT</td>
<td>1.25</td>
<td>-</td>
<td>42.71</td>
<td>0.08956</td>
<td>8.364</td>
<td>7.637</td>
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</tr>
<tr>
<td>0.5 CEC-DDTMA</td>
<td>1.40</td>
<td>0.44</td>
<td>28.98</td>
<td>0.10738</td>
<td>14.80</td>
<td>8.504</td>
<td></td>
</tr>
<tr>
<td>1.0 CEC-DDTMA</td>
<td>1.80, 1.41</td>
<td>0.77</td>
<td>17.67</td>
<td>0.09339</td>
<td>21.33</td>
<td>9.357</td>
<td></td>
</tr>
<tr>
<td>1.5 CEC-DDTMA</td>
<td>1.80, 1.49</td>
<td>0.81</td>
<td>16.27</td>
<td>0.09334</td>
<td>23.08</td>
<td>8.755</td>
<td></td>
</tr>
<tr>
<td>2.0 CEC-DDTMA</td>
<td>1.84, 1.55</td>
<td>0.86</td>
<td>15.97</td>
<td>0.08788</td>
<td>22.16</td>
<td>8.630</td>
<td></td>
</tr>
<tr>
<td>0.5 CEC-DDDMA</td>
<td>1.75</td>
<td>0.45</td>
<td>12.47</td>
<td>0.06926</td>
<td>22.19</td>
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<td></td>
</tr>
<tr>
<td>1.0 CEC-DDDMA</td>
<td>2.69, 1.87, 1.37</td>
<td>0.77</td>
<td>12.83</td>
<td>0.07551</td>
<td>23.65</td>
<td>11.09</td>
<td></td>
</tr>
<tr>
<td>1.5 CEC-DDDMA</td>
<td>3.11, 2.15, 1.52</td>
<td>1.16</td>
<td>2.095</td>
<td>0.01809</td>
<td>34.58</td>
<td>11.97</td>
<td></td>
</tr>
<tr>
<td>2.0 CEC-DDDMA</td>
<td>3.17, 1.72, 1.51</td>
<td>1.43</td>
<td>0.390</td>
<td>0.00327</td>
<td>34.04</td>
<td>15.82</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Surfactant loading expressed in CEC of montmorillonite (100g) from Thermogravimetric analysis (TG). \(^b\)Barrett-Joyner-Halenda (BJH) desorption cumulative pore volume of pores between 1.7 and 300 nm in diameter. \(^c\)Adsorption average pore diameter (4V/A by BET). \(^d\)BJH desorption average pore diameter.
This is in a good agreement with the pore diameter obtained from the Barrett-Joyner-Halenda (BJH) desorption isotherm in Table 7.1. A similar result was also found by Gregg and Sing [24].

From Table 7.1, the surface area and pore size of the organoclays decreased gradually with increasing surfactant loading and this shows an increased packing arrangement of the organoclays as well as the change in the arrangement of surfactant molecules within the interlayer space from being parallel to the silicate surface to being at certain angles to the silicate surface [25, 26]. It appears that the size of the surfactant molecules is responsible for the higher packing arrangement observed. Thus, the structures of the organoclays are highly dependent on the loaded surfactant molecules. Hence, organoclays prepared at higher surfactant loadings explore more potential sorption sites in the interlayer space, which lead to increased adsorption and desorption pore diameters. Based on the results, two different groups were created. Group I has organoclays with less than 1.0 CEC (< 1.0 CEC), while Group II has organoclays prepared over 1.0 CEC (≥ 1.0 CEC). These two groups are well-resolved in the obtained XRD patterns and the arrangement of surfactant molecules in the organoclays is an important key in determining the adsorption mechanisms.

7.3.1.3 XPS

The surface chemical composition of MMT and the organoclays were analysed using XPS and the results summarised in Table 7.2 showed that major elements such as aluminium, silicon, iron, and magnesium are present in the organoclays. Appreciable amounts of carbon and oxygen are detected due to adsorbed CO₂ under atmospheric conditions [27]. From the survey scan, trace amounts of magnesium and iron are observed in the organoclays and the sodium peak disappeared when cationic surfactants are intercalated in the interlayer space of the clays. Similar results were observed in the previous study [21, 28]. The prominent peaks of carbon and silicon were noticed in both materials and the ratio of C/Si increased with increasing surfactant loadings: 1.09 (1.0 CEC-DDTMA) < 1.13 (2.0 CEC-DDTMA) < 2.34 (1.0 CEC-DDDMA) < 4.79 (2.0 CEC-DDDMA). On the other hand, the obtained ratio of Al/Si decreases as follows: 0.42 (MMT) > 0.38 (1.0 CEC-DDTMA) ≈ 0.35 (0.2 CEC-DDTMA) > 0.31 (1.0 CEC-DDDMA) >> 0.08 (2.0 CEC-DDDMA) in accordance with the fact that increasing the surfactant loading leads to an increase in
the interlayer space of organoclays which decreased the distance between the octahedral sheet and two siloxane tetrahedral sheets of MMT. To investigate the structural changes in the clays, high resolution spectra of these elements were also obtained. The changes in the binding energies of Al 2p, Si 2p, and C 1s are summarised in Table 7.2. The reduced binding energies of Si 2p and Al 2p from the high resolution spectra indicate changes in the structures of the organoclays intercalated with surfactant molecules. Unlike the decreasing bonding energies in the Si and Al spectra, the binding energy of C-C in C spectra gradually increased, and this shows that the local environment of surfactant has a prominent effect on the binding energy. However, the binding energy of C-N was independent of the surfactant loading and this is similar to the binding energy obtained for C 1s in the C-N bond as a result of electrostatic interaction between the headgroups (nitrogen) of the alkyl chains and the negatively charged clay surface. The conformational changes in surfactant molecules within the organoclays are supported using the molecular mechanical model present in the following section.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al 2p</th>
<th>Si 2p</th>
<th>C 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Binding energy/ eV</td>
<td>Binding energy/ eV</td>
<td>Binding energy/ eV</td>
</tr>
<tr>
<td>DDTMA</td>
<td>0.5 CEC</td>
<td>71.57</td>
<td>99.73</td>
</tr>
<tr>
<td></td>
<td>1.0 CEC</td>
<td>70.76</td>
<td>98.85</td>
</tr>
<tr>
<td></td>
<td>1.5 CEC</td>
<td>70.71</td>
<td>98.81</td>
</tr>
<tr>
<td></td>
<td>2.0 CEC</td>
<td>70.71</td>
<td>98.75</td>
</tr>
<tr>
<td>DDDMA</td>
<td>0.5 CEC</td>
<td>71.37</td>
<td>99.87</td>
</tr>
<tr>
<td></td>
<td>1.0 CEC</td>
<td>70.67</td>
<td>99.41</td>
</tr>
<tr>
<td></td>
<td>1.5 CEC</td>
<td>70.82</td>
<td>98.69</td>
</tr>
<tr>
<td></td>
<td>2.0 CEC</td>
<td>70.95</td>
<td>98.87</td>
</tr>
</tbody>
</table>

7.3.1.4 FT-IR

FT-IR is one of techniques used to probe the molecular conformation of intercalated surfactants within the organoclays. The infrared spectra of unmodified MMT and the organoclays are shown in Figure 7.3.

In Figure 7.3, the OH stretching region in 3700 – 3000 cm⁻¹ is characterised by two bands and the sharp intense peak at 3631 cm⁻¹ is assigned to the structural OH group.
in the clay and the broad band between 3500 – 3000 cm\(^{-1}\) is ascribed to hydrogen bonded water molecules adsorbed within the interlayer space of the clay. It was noticed that the broad band was relatively dependent on the concentration of the surfactant and the intensity of the bands gradually decreased as the surfactant loading increased due to the fact that water molecules are replaced with the loaded surfactants in the interlayer space of MMT. This shows that the internal surface property of the clays had become more hydrophobic.

Figure 7.3 FT-IR spectra of MMT and modified MMT intercalated with DDTMA (a) and DDDMA (b)
Other characteristic peaks investigated are in the region between 2900 – 2700 cm\(^{-1}\) and these were assigned to the CH stretching vibrations from surfactant molecules. In addition, antisymmetric and symmetric stretching modes were observed for the organoclays modified with DDTMA and DDDMA. It was found that both CH stretching modes of amine chains were shifted toward lower wavenumbers with increasing surfactant loadings; 2928 to 2927 cm\(^{-1}\) and 2855 to 2849 cm\(^{-1}\) in organoclays intercalated with DDTMA (Figure 7.3a), and 2927 to 2921 cm\(^{-1}\) and 2852 to 2851 cm\(^{-1}\) in organoclays intercalated with DDDMA (Figure 7.3b), respectively. According to the previous findings of He et al. [29] and Wang et al. [30], the CH stretching bands are relatively sensitive to the conformational changes in the chain within the interlayer and the shift to lower wavenumber in stretching mode leads to the formation of all-\textit{trans} conformation in organoclays. It was also noted that the antisymmetric and symmetric CH stretching peaks for organoclays intercalated with DDDMA were at lower wavenumbers, which may be due to the length of the chain and the structure of the surfactant molecules. The large DDDMA molecule tends to contribute to more ordered conformation than the DDTMA molecule. A similar result was found in the previous study by Sarkar et al. [15]. The structural conformation of DDTMA and DDDMA molecules intercalated in the interlayer space of MMT was further investigated using computational modelling.

### 7.3.2 Molecular mechanical modelling

The structure of the tetrahedral-octahedral-tetrahedral sheet (TOT) layer in MMT was described in Figure 7.4 after geometry optimisation using molecular mechanical calculation (MM calculation).

![Montmorillonite TOT layers after geometry optimisation](image)
The surfactant reagent molecules in the interlamellar space affected the layer distance of the MMT. The calculated energy profile of the organoclays intercalated with DDTMA and DDDMA was obtained and presented in Figures 7.5 and 7.6.

In Figure 7.5, it can be observed that the system energy showed a global minimum at \( d = 15 \, \text{Å} \), and the organoclay compounds prepared at CEC = 0.25 and 0.5 CEC can be considered as stable. When the CEC was over 1.0 CEC (i.e. \( \geq 1.0 \) CEC), there were two overlapping XRD peaks at 14 – 15 Å and 18 Å, which indicate the presence of two different structures. The basal spacing increased with the CEC and the forces holding the complex together show a local minimum (inflection point) at a basal distance at 18.5 Å. The TOT-TOT layers in the TOT-DDTMA-TOT complex system influenced each other when the basal spacing was at 20 – 21 Å (the calculated values are given with a solid line, while the broken line represents the Lennard-Jones type function in this region). Since the distance between the TOT layers is higher than the range of the attractive forces, only the TOT-DDTMA interactions were investigated in this study.

The same method was applied in order to describe and calculate the energy profile of organoclays intercalated with DDDMA cation (in Figure 7.6). The minimum system energy of the organoclays was obtained at a layer distance of 14.5 Å, which is close
Figure 7.6 Calculated energy profile for MMT-DDDMA complex and the structures by MM method
to the experimental value obtained by XRD. The structure of the DDDMA cation between the TOT layers basically depends on the \( d(001) \) value. When only a limited space is available, the two long chains of DDDMA give a torsional angle of 180° and the reagent was present in a monomolecular layer. With increase in the basal distance \( (d(001) > 17.5 \, \text{Å}) \) at 1.5 and 2.0 CEC, the torsional angle may be close to 60°. It should be noted that structural changes caused by changes in the torsional angle can only be taken into consideration if the interlayer distance is at least twice as large as the length of the DDDMA cation. Thus, the position of the DDTMA and DDDMA cation in the interlamellar gallery as a function of CEC was investigated and summarised in Figures 7.7 and 7.8.

As shown in Figure 7.7, the reagent was present in an ordered monolayer with a head-to-tail position up to CEC ≤ 0.5 CEC. Upon increasing the CEC, the cations get closer to each other until the attraction and repulsive forces are in equilibrium. When the repulsive forces prevail, the reagent molecules were arranged in a double layer which shows the presence of at least two different structures (with \( d \) values of 14 and 18 Å). Upon increasing the CEC level further, a significant interaction exists between the molecules resulting in a condensed, rather than a quasi-crystalline phase. This supposition is in harmony with the decreased intensity and broadening of the XRD peaks. When the CEC reached 2.0 CEC, the interaction between the TOT-DDTMA structures prevails. This combination of experimental and molecular mechanical calculations is beneficial for nanostructures since the experimental data can be quasi-validated by computation methods. The described structural variations of DDDMA cations in the interlamellar space are summarised in Figure 7.8. This shows that the DDDMA cation was present as a monolayer with torsional angle of 180° when CEC = 0.25 (14.5 Å of basal spacing). Upon increasing the surfactant loading, the reagent took up an alternating-type of pattern. When CEC reached 1.0, the increased basal spacing of the reagent gives a torsional angle of 90°, present in a double layer pattern (at 19.5 Å) and further close to 60°. If the TOT layer distance is big enough (CEC > 1), the two dodecyl chains of the DDDMA reagent can take up a “V” shape. This conformation can only be an alternative to the case when the reagent is present in a double layer (torsional angle is 180°) if hydration is completely ignored. It should be noted that if torsion is taken into account, the computational time is highly increased for a particular case (i.e. for a high atomic number reagent in
the interlamellar gallery) the applicability of the model would be significantly restricted. When “free” reagent torsion is considered, the required space at torsional angles of 90 – 60° is at 18 – 20 Å. In conclusion, the realistic situation is that in the case of CEC ≥ 1 mixed structures are present in the interlamellar space. This is supported by XRD measurements (cif. Figure 7.1, XRD pattern).

![Figure 7.7 The geometry of DDTMA in the interlamellar space](image)

![Figure 7.8 Structural variations of DDDMA cation in the interlamellar space](image)
The proposed computational models show that the system energy of the basal spacing and the corresponding geometry of the surfactants at minimum or a local minimum are well approximated. The use of the MM calculation complements and corroborates the XRD data as the MM calculations facilitate the visualisation of the conformational changes of the surfactant molecules and enhance the understanding of the results from XRD. This computational method is also beneficial for monitoring and validating the experimental data for nanostructures.

7.3.3 Adsorption experiments

7.3.3.1 Effect of surfactant loading
Since the structural changes in MMT and the modified clays were revealed, the capacities of the materials as a potential adsorbent for the removal of PCP and PNP from aqueous solutions were investigated. The maximum percentage of removed PCP and PNP by the organoclays are shown in Figure 7.9.

The amount of PCP and PNP removed by the unmodified MMT is relatively lower (about 4.8 and 44.0 %, respectively, not presented in Figure 7.9) and increased gradually in the organoclays at higher CEC levels. This result proves that the modified clays are favourable adsorbents for the uptake of phenolic compounds. The obtained results are also in good agreement with the assumption that organoclays with larger interlayer space will accommodate more phenolic compounds. In particular, organoclays intercalated with the di-cationic surfactant, DDDMA are more efficient adsorbents than those with DDTMA. These initial adsorption results show that the packing density of organoclays as well as the size of surfactant molecules are critical factors to consider in improving the adsorption capacity of adsorbents. To be an efficient adsorbent in the environment, the phase for the removal of explored phenolic compounds in the aqueous medium is vital and the kinetic study on the adsorption of PCP and PNP in aqueous solutions using organoclays was performed and described in the following section.
Figure 7.9 Percentage of PCP and PNP adsorbed by the organoclays
Figure 7.10 Effect of agitation time for the adsorption of PCP (a) and PNP (b) by organoclays (100 mg/L of PCP and PNP)
Figure 7.11 Intra-particle diffusion for the adsorption of PCP (a) and PNP (b)
7.3.3.2 Kinetics

This section investigates the effect of agitation time on the amount of phenolic compounds adsorbed onto the organoclays at room temperature (described in Figure 7.10). It appears that the amount of adsorbed PCP and PNP is relatively proportional to the agitation time. In Figure 7.10 (a), the initial amount of adsorbed PCP by organoclays intercalated with DDTMA increased gradually up to 60 mins and slowly reached the maximum concentration within 80 mins. However, the amount of adsorbed PCP by the organoclays intercalated with DDDMA slowly increased to the maximum concentration within 60 mins. The removal of PNP occurred in a similar way except the amount of time required to reach the maximum concentration is longer as shown in Figure 7.10 (b).

Several kinetic models including pseudo-first order equation, pseudo-second order equation, and intra-particle diffusion model have been used to explain the sorption system between liquids and solids. For example, the intra-particle diffusion model suggested by Weber and Morris [31] is applied to support the involvement of diffusion mechanisms in the adsorption process. The intra-particle diffusion is involved when the plot is linear and it is the controlling step if the line passes through the origin. Figure 7.11 shows that several steps are observed: (i) an initial curve, (ii) linear step, and lastly (iii) a plateau. According to the same studies [32, 33], the initial curve and the linear process step are results of the bulk diffusion and intra-particle diffusion. This means that intra-particle diffusion is involved in the current study but it is not a controlling step during the adsorption process.

The parameters of the kinetic models (pseudo-first, -second, and intra-particle diffusion) were calculated and summarised. The obtained high correlation coefficients for the pseudo-second order kinetic model demonstrated that the adsorption of PCP and PNP onto the organoclays followed the pseudo-second model better than the pseudo-first order kinetic model in this study. In Figure 7.10, a straight line was obtained over the whole range of time investigated. Values of $q_e$ shown from the figure indicated that the organoclays have larger uptakes of PNP than PCP. The adsorption rate $k_2$ value decreased with increasing surfactant addition and this is caused by the pore size distribution or pore-blocking effect [34]. This is in good agreement with the pore size obtained from BET (see Table 7.1). The smaller pore size observed was because the loaded surfactant molecules blocked the pores.
conclusion, the excellent pseudo-second order model fit observed data and confirmed that chemisorption controlled the rate controlling adsorption step of both PCP and PNP compounds by the organoclays intercalated with DDTMA and DDDMA [35].

Figure 7.12 Effect of the final pH on the adsorption of PCP (a) and PNP (b)
7.3.3.3 Effect of pH

This study investigates the adsorption of phenolic compounds at varied pH environments in order to determine the optimum pH conditions for the adsorption of PCP and PNP. The investigated PCP and PNP are present as weak acids in aqueous solution with dissociation constants (pKₐ) of 9.18 and 7.15, respectively [7]. The applied pH condition was in the range from 2 to 8 or 9 and the initial concentration of PCP and PNP solution was 100 mg/L. The obtained results for the uptake of PCP and PNP by the organoclays are presented in Figure 7.12.

In Figure 7.12, it is clearly seen that the adsorption of phenolic compounds are dependent on the pH value, and in particular, the adsorption of PCP and PNP was improved under acidic rather than basic conditions. The maximum adsorption was maintained when the pH of 5 is reached. When the pH rose beyond 6, the adsorption of PCP gradually decreased while that of PNP significantly dropped. It is noticed that at 2.0 CEC the organoclays prepared with DDDMA adsorbed larger amounts of the phenolic compounds over the entire pH range investigated. These results can be explained by (i) the surface charge of clays and (ii) degree of dissociation of the phenolic compounds.

On the external structure of MMT, the siloxane group (Si-O) in the tetrahedral sheets is weaker and becomes Si-O bond which further converts to Si-OH depending on the variation of pH. At a higher pH condition, the surface functional group is fully or partially deprotonated which leads to an increase in the negative charge on the surface. The surface charge properties were confirmed from the zeta potential reported in some previous studies [34, 36, 37]. PCP and PNP were present as weak acids and they mainly exist as neutral molecules when the pH of solution goes below the pKa (pH < pKa), while the phenols prevail as phenolate anions when the pH goes beyond the pKa [38]. From the dissociation condition of the phenolic compounds at varied pH, the neutral molecules of PCP and PNP tend to be adsorbed more effectively onto the modified clays than the anionic species. In particular, the surfactant molecules in the interlayer space of the organoclays tend to act as an efficient partition medium for the removal of PCP and PNP via hydrophobic interaction and Van der Waals interaction under acidic environmental conditions.
Table 7.3 Langmuir and Freundlich isotherm parameters for the adsorption of PCP and PNP

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
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<tr>
<td></td>
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<td>$q_m$ (mg/g)</td>
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<td>35</td>
<td>62.893</td>
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When the pH of the solution became alkaline the adsorption of PCP and PNP decreased as a result of the electrostatic repulsive force between the increased negative charged on the clay surface and the anionic forms of PCP and PNP. It is interesting to observe that the organoclays intercalated with the two long alkyl chained surfactants are effective adsorbents. In the paper by Sakar et al. [37], an increase in the total organic carbon contents contributed to the increased hydrophobic lateral interactions. Thus, the longer alkyl tails of the surfactants of the two long alkyl chained surfactants develop more positive charge on the clay surface by shielding the negative charge. This leads to the attraction of the anionic forms of PCP and PNP even at the basic conditions. Therefore, the organoclays with higher surfactant loadings and those prepared with DDDMA are less influenced by pH environments compared with the organoclays with lower surfactant loading and those intercalated with DDTMA. Several possible mechanisms including hydrogen bonding, hydrophobic interaction and Van der Waals interaction may be responsible for the adsorption of phenolic compounds reported in this study. The operating mechanism was thus discussed using several possible adsorption isotherm models.

7.3.3.4 Mechanism of adsorption of the phenolic compounds by organoclays
To have better quantitative understanding of the mechanisms involved in the adsorption of phenolic compounds, two classical adsorption isotherm models, namely: Langmuir and Freundlich adsorption isotherms were applied [36, 37] and discussed as follows.

Based on the equilibrium equations for both isotherms, the required parameters were obtained and presented in Tables 7.3. The results show that the obtained $R^2$ values showed that both PCP and PNP were better fitted into the Freundlich isotherm model than the Langmuir model. This suggests that the adsorption of both phenolic compounds by organoclays involves multilayer adsorption rather than monolayer adsorption. The Freundlich parameters including $n$ and $K_F$, assigned to the measurement of the adsorption strength of the phenolic compounds and the binding affinity constant provide more substantial information on the adsorption mechanism. The value of $n$ observed for the adsorption of PCP solution is smaller than 1 ($n < 1$) and this indicated that the adsorption system is more favourable at higher concentrations of PCP. On the other hand, the adsorption process for PNP solution is
effective over the entire range of concentrations based on the $n$ value higher than 1 ($n > 1$) [39].

The binding affinity constant, $K_F$ shows that the index relatively corresponded to the increased rate of surfactant loading as well as the size of surfactant molecules. The $K_F$ value in the adsorption of both PCP and PNP decreased as the temperature increased. However higher $K_F$ values were obtained in the adsorption of PNP than of PCP, and again these fitted well with the experimental data.

Several mechanisms such as hydrophobic interaction, hydrogen bonding, and electrostatic interaction may be involved in the adsorption of phenolic compounds. At CEC less than 1.0, the loaded surfactant replaced the exchangeable cations mainly enter the interlayer space of MMT. When the CEC exceed 1.0 CEC, the surfactants loaded filled the interlayer space but also on the external space of the clays, and the loaded surfactant molecules formed strongly attract the undissociated phenolic molecules through hydrophobic interaction. On the other hand, the dissociated phenolic anions tend to interact with the surfactant cations on the external surface of the clays via electrostatic interaction. Due to the larger size of the surfactant, the organoclay intercalated with DDDMA is likely to involve mainly partitioning mechanism than that intercalated with DDTMA. Thus, the organoclays have a greater capacity for the adsorption of PNP rather than PCP in the aqueous solutions. It is evident from the relatively decreased $K_F$ values (in Table 7.3) that a higher affinity of PNP than PCP onto the adsorption sites of the organoclays occurred due to their different polarity levels [7, 34]. Another mechanism suggested in this adsorption system may be donor-acceptor complex formation between the solute and adsorbent. In this respect, the higher affinity of PNP than of PCP for the organoclays leads to stronger hydrogen bonding [7]. Hence, the stronger hydrophobic properties of PNP over PCP results in a higher affinity for the organoclays, which can lead to have higher sorption energy. The decreased $K_F$ values in terms of temperature effect from 23 to 35 °C are also good indications that the adsorption processes for PCP and PNP involve exothermic reactions.
7.4 Conclusions

The current study investigated the use of organoclays for environmental applications in terms of removing phenolic compounds from aqueous solutions. The organoclays were prepared from hydrophilic montmorillonite by the intercalation of cationic surfactants (DDTMA and DDDMA as an example of mono- and di- alkyl chain surfactants). Their structural properties were examined using various techniques. As the surfactant loading increases, structural changes in the DDTMA and DDDMA molecules occurred, leading to expanded basal spacings. It was found that the size of surfactants highly influenced the degree of expansion in the interlayer space of the clays.

The conformational changes of the surfactant molecules within the interlayer space were visually demonstrated using molecular mechanical calculation, which enhanced the understanding of the results obtained from characterisation methods such as XRD and surface analysis. The characterised organoclays were tested for their adsorption capacities for the uptake of PCP and PNP from aqueous solutions and the organoclays were found to be more efficient than the unmodified clay due to the hydrophobicities. The organoclays intercalated with higher surfactant loading as well as those intercalated with DDDMA tend to afford better uptakes of the phenolic compounds. However, the process of reaching the equilibrium is slower as more surfactants are loaded due to pore blocking effect. The sorption system fitted well with pseudo-second order model and intra-particle diffusion (but not as the controlling step). The adsorption of PCP and PNP were best explained by Freundlich isotherm rather than Langmuir isotherm, which indicates the presence of multilayer sorption including hydrophobic interaction, hydrogen bonding, and electrostatic interaction. In particular, the loaded surfactant molecules in the interlayer space formed partition phases, which resulted in the attraction of the phenolic molecules strongly through hydrophobic interaction. Furthermore, the adsorption system of phenolic compounds by organoclays intercalated with DDDMA is likely to involve mainly partitioning mechanism than that intercalated with DDTMA. Hence, the organoclays intercalated with DDDMA prove to be better adsorbents for the removal of PCP and PNP and they are more likely to remove PNP over PCP. This study revealed the potential utility of the organoclays as adsorbents for the uptake of industrial pollutants in environment applications. To advance the use of organoclays
as adsorbents in real industrial and environmental practice, the re-use of surfactant or re-generation of organoclays warrants further investigations to reduce any environmental risks as well as treatment cost to the industry.

Acknowledgement
The authors gratefully acknowledge and express gratitude for the financial and infrastructural assistance provided by Queensland University of Technology (QUT). The Australian Research Council (ARC) is thanked for funding some of the instrumentation.

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7.5 References


CHAPTER 8
APPLICATION OF ORGANOCLAYS FOR
THE ADSORPTION OF
PHARMACEUTICAL AND PERSONAL
CARE PRODUCTIONS (PPCPs)

This paper was originally submitted:

Yuri Park, Zhiming Sun, Godwin A. Ayoko and Ray L. Frost, Bisphenol A sorption
by organo-montmorillonite: Implications for the removal of organic
contaminants from water. Submitted to Chemosphere.
PREFACE
The previous paper indicated that organoclays were effective adsorbents for the removal of phenolic compounds. In particular, the organoclays intercalated with DDDMA adsorbed a large amount of phenolic compounds and the significance of the size of surfactants was emphasised. A similar finding was found that both organoclays intercalated with DDTMA and DDDMA were better adsorbents for the removal of PNP than PCP due to different hydrophobic properties. Those two papers in Chapters 6 and 7 clearly explored the potential of organoclays as adsorbents for the removal of phenolic compounds from industrial effluents.

Considering the previous results, it may be useful to test the organoclays for the removal of emerging pollutants. This chapter included the adsorption of Bisphenol A (BPA), a suspected endocrine disrupting agent, using the organoclays intercalated with HDTMA, DDTMA and DDDMA. Different experimental conditions (e.g. agitation time, temperature, pH, different concentrations of solutions) were applied to assess, improve the adsorption of BPA, and comprehensively describe the mechanisms involved in the adsorption process. The amount of adsorbed BPA by the organoclays was compared with those reported for other materials in order to evaluate the potential of organoclays for the removal of BPA from contaminated water.
STATEMENT OF CONTRIBUTION OF CO-AUTHORS

The authors listed below have certified* that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and
5. they agree to the use of the publication in the student’s thesis and its publication on the QUT ePrints database consistent with any limitations set by publisher requirements.

In the case of this chapter:

Bisphenol A sorption by organomontmorillonite: Implications for the removal of organic contaminants from water *Submitted to Chemosphere*

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<tr>
<td>Yuri Park (candidate)</td>
<td>Developed the experimental design, conducted the experiments, analysed data, and wrote the manuscript.</td>
</tr>
<tr>
<td>Zhiming Sun</td>
<td>Conducted experiments and analysed analysis</td>
</tr>
<tr>
<td>Godwin A. Ayoko* (Principal Supervisor)</td>
<td>Assisted in the experimental design, data analysis and edited the manuscript.</td>
</tr>
<tr>
<td>Ray L. Frost (Associate Supervisor)</td>
<td>Assisted in the experimental design, data analysis and edited the manuscript.</td>
</tr>
</tbody>
</table>

Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

Prof Godwin Ayoko [Signature] 14/10/2013

Name Signature Date
8.1 Introduction

The growing population and urbanization of society has resulted in an increased production and dispersion of toxic chemicals, including the endocrine-disrupting chemicals (EDCs) into the environment [1]. Many EDCs including natural estrogens (e.g. estrone (E1), 17β-strodial (E2), and estriol (E3)), synthesised estrogen (e.g. ethinylestradiol (EE2)), and industrial compounds (e.g. bisphenol A (BPA) and nonylphenol) are organic compounds with one or more phenolic groups. Due to their structures and physicochemical properties, these molecules can naturally occupy the high affinity binding acceptor sites of the hormone receptors. This result in disrupted endocrine systems and contributes to environmental risks for animals and humans [2-4].

EDCs are removed from sewage through wastewater treatment plants (WWTPs) [5, 6]. However, due to their complex structures and low biodegradability [7-9], they are not removed completely through biological treatment and can still be detected in the discharge of WWTPS. Since these molecules have been detected in wastewater, groundwater, sediments, and even drinking water, EDCs are of great public and environmental concerns [10-13]. BPA is widely used as a monomer for the manufacture of polycarbonates and epoxy resin in the plastic industry. Because of its ubiquitous nature in the environment and its negative effects to human health and organisms [14, 15], it is considered as one of high priority compounds that must be monitored and removed from the environment. Hence, BPA is selected as the test molecule in this study.

![Figure 8.1 Structures of four EDCs (a) estrone (E1), (b) 17β-strodial (E2), (c) estriol (E3), and (d) bisphenol A](image)

Figure 8.1 Structures of four EDCs (a) estrone (E1), (b) 17β-strodial (E2), (c) estriol (E3), and (d) bisphenol A
There is a clear need for the development of simple and highly efficient methods for the safe remediation of organic substrates. Some techniques, including adsorption [6, 16, 17], membrane filtration [18, 19], electrochemical technique [20], and catalysis/photocatalysis [21-25] have been proposed for the removal of these contaminants. The approach reported in this study is adsorption process by organooclays which has some advantages over the other techniques. These include their relatively low operational cost, ease of operation, and production of less secondary products [26]. In recent years, adsorption by organooclays is widely used for the removal of organic and inorganic contaminants in waters [27-30] because the use of such low-cost adsorbents which utilises materials that naturally available is economically feasible.

Among many materials that are naturally abundant, clay minerals are potential adsorbents due to their low cost, environmental stability, high adsorption/absorption, and ion exchange properties [31-33]. In particular, montmorillonite (MMT) is widely used because of its high cation exchange capacity (CEC), swelling property, and high surface area [33]. However, one of the drawbacks of clay minerals is their hydrophilic properties and this structural property makes them ineffective for the removal of organic pollutants. The permanent negatively charged clay surface can be modified by cationic surfactant molecules, and through ion exchange, hydrophilic clays can be converted to hydrophobic organooclays. We previously demonstrated that these organooclays are effective adsorbents for the removal of phenolic compounds. Given that BPA has two phenolic groups, we reasoned that the organooclays will be good adsorbents for removing BPA from aqueous media. Thus, the aims of this work are to: (a) investigate the adsorption properties of organooclays toward BPA, (b) demonstrate their potential for the uptake of BPA from aqueous solutions under different experimental conditions such as agitation time, pH, temperature, and different BPA concentrations, (c) evaluate the mechanisms involved in the adsorption of BPA by the organooclays, and (d) compare the results with those obtained when different adsorbents and other methods were used. To the best of our knowledge, the removal of BPA by organooclays has not been investigated previously, and this work demonstrates the potential performance of the organooclays as adsorbent for the uptake of the industrial by-products such as BPA from aqueous solutions.
8.2 Materials and Experimental methods

8.2.1 Materials
Pure MMT was purchased from Sigma-Aldrich and used without further purification. Its cation exchange capacity (CEC) is 76.4 meq/100 g. Different types of cationic surfactants were used as examples of mono- and di-alkyl cationic surfactants in this study and these are: (i) dodecytrimethylammonium bromide (denoted as DDTMA, C\textsubscript{15}H\textsubscript{34}NBr, FW: 308.34), (ii) hexadecyltrimethylammonium bromide (denoted as HDTMA, C\textsubscript{19}H\textsubscript{42}NBr, FW: 364.46), and (iii) didodecyldimethylammonium bromide (denoted as DDDMA, C\textsubscript{26}H\textsubscript{56}NBr, FW: 462.65) and all of which were purchased from Sigma-Aldrich and used without further purification.

8.2.2 Synthesis and Characterisation of organoclays
The organoclays were prepared and characterized by various techniques including powder X-ray diffraction (XRD), surface area measurement (BET method), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA), and their structural properties and characteristics were already described in the previous studies by Park et al. [34, 35].

8.2.3 Batch adsorption experiments
BPA [2,2-bis(4-hydroxyphenyl)propane] was purchased from Sigma-Aldrich and used to investigate the adsorption capacities of MMT and the modified organoclays. BPA solution was initially prepared as a stock solution (5000 mg/L) in ethanol due to its low solubility in water, and it was further diluted in water for the preparation of different BPA concentrations. From the initial experiment to determine the amount of adsorbent required, 0.2 – 0.3 g of the adsorbents were placed in sealed 50 mL centrifuge tubes with 40 mL of a BPA solution in the appropriate concentration (which ranged from 5 to 500 mg/L). The bottles were placed in a rotary shaker and/or a shaking water bath for 12 hr at the appropriate temperature. The initial pH of BPA was close to pH 4 – 5. After shaking, the mixture was filtered through 0.22 µm filters (hydrophilic PTFE membrane) and the supernatants were analysed by a high-performance liquid chromatography (HPLC, Agilent HP 1100) system coupled with a Luna 5µ C18 column (Phenomenex Pty Ltd) and a UV detector. A mobile phase mixture containing 70 % methanol and 30 % water at a flow rate of 0.1 mL/min and 40 µL of injection volume was used for this experiment and the detector
was operated at 278 nm. To undertake the adsorption kinetics, the adsorbents were added with an initial BPA concentration (100 mg/L) at room temperature in order to determine the minimum time to reach the equilibrium concentration. The concentrations of BPA were measured at different time intervals from 10 to 240 min. To evaluate the thermodynamic properties, the adsorbed concentrations of BPA solution by the organoclayes were obtained at 296.15, 308.15, and 318.15 K, respectively. Similarly, the effect of the pH on the adsorption of BPA (with initial BPA concentration of 100 mg/L) was studied by adjusting the pH of BPA solution (using either diluted 0.1 M HCl or NaOH). The quantity of the adsorbed BPA was calculated using the following equation.

\[ q_e = \frac{V(C_i - C_e)}{M \times 1000} \]

where, \( q_e \) is the amount of solute adsorbed on the adsorbent (mg/g), \( C_i \) is the initial concentration of the solute (mg/L), \( C_e \) is the equilibrium concentration of the solute (mg/L), \( V \) is the volume (mL), and \( M \) is the mass of the adsorbent (g).

8.3 Results and discussion

8.3.1 Initial adsorption of BPA by MMT and organoclays

The characterised MMT and organoclayes intercalated with DDTMA, HDTMA, and DDDMA, which were already described in the previous studies [34] were evaluated for their adsorption capacities for the uptake of BPA from aqueous solutions. Maximum removal of BPA was obtained after 12 hr agitation time while the amount of adsorbed BPA by unmodified MMT was 6.3 %, which is negligible. At 1.0 CEC level, the adsorption of BPA was 96.3 and 98.9 % by the organoclayes intercalated with DDTMA and HDTMA, respectively. In particular, the organoclayes prepared from the di-cationic surfactant, DDDMA, adsorbed about 99.5 % of BPA solution at 1.0 CEC. The amount of BPA adsorbed by the organoclayes intercalated with higher surfactant loadings slightly increased up to 2.0 CEC. This indicates that the organoclayes are more effective than the unmodified MMT for the uptake of BPA and that the efficiency in the adsorption of BPA by the organoclayes was relatively influenced by the size of the surfactant molecules as well as the level of surfactant loadings. The initial adsorption results indicate that adsorption by organoclayes is
effective for the removal of BPA and the next investigation was based on the determination of the phase for the uptake of BPA.

**Figure 8.2** Effect of agitation time on the adsorption of BPA by MMT and organoclays

**Figure 8.3** Test of pseudo-second order model for sorption of BPA by MMT and organoclays
8.3.2 BPA adsorption kinetics – Effect of agitation time

To obtain a better understanding of the mechanisms in the adsorption of BPA, the relationship between the agitation time and the amount of BPA adsorbed onto the MMT and organoclays was investigated as presented in Figure 8.2.

It appears that the agitation time affected the amount of adsorbed BPA. The adsorption of BPA by both MMT and the organoclays increased quickly in the first 20 min and rose slowly up to equilibrium concentration within 1 hr.

To investigate the mechanisms involved in the adsorption process, two conventional kinetic models (pseudo-first order and pseudo-second order) were applied to analyse the experimental data. The pseudo-first order and pseudo-second order models can be expressed using equation [36] described in Chapter 6. The diffusion mechanism can also be explained using intra-particle diffusion [37], which is presented in Chapter 6.

Table 8.1 summarises the kinetic parameters and correlation coefficients for the adsorption of BPA by MMT and organoclays. It is shown that the pseudo-second order kinetic model fitted better than the pseudo- first order model in this study (see Figure 8.3). A similar finding was reported in the adsorption of BPA on graphene [16]. This suggests that the rate-limiting step may be chemical sorption or chemisorption and the model provides the best correlation of the experimental data.

In addition, the lower than 1 coefficients ($R^2 < 0.99$) observed in the linear relationship from the intra-particle diffusion modelling may suggest that intra-particle diffusion was not involved and it is not a controlling step during the adsorption of BPA in this study.

<table>
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<th>Sample</th>
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8.3.3 BPA adsorption isotherms

Several adsorption isotherm models are usually applied in order to have a better understanding of the adsorption process of absorbates. In this study, the two classic physical isotherm models: Langmuir and Freundlich isotherms were applied and discussed as follows.

The equations used for the Langmuir and the Freundlich models are described in the Chapter 6. The Langmuir isotherm describes the interaction between the adsorption of the adsorbate and the surface of the adsorbent. It assumes that a monolayer adsorption occurs on a homogeneous surface. Once the adsorption occurs at the specific sites in the adsorbent, no further adsorption occurs at the sites. Thus, the adsorption to the surface is strongly related to the driving force and surface area [38]. On the other hand, the Freundlich model is based on the use of an empirical expression to describe the adsorption theory and this model assumes that a multilayer adsorption occurs on the heterogeneous surface or surface supporting sites of varied affinities [39]. This model is capable of predicting the infinite surface coverage involving the multilayer adsorption of the surface.

Table 8.2 Isotherm parameters for the adsorption of BPA by organoclays

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<td>$q_m$ (mg/g)</td>
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<td>0.62</td>
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<td>35</td>
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<td>23</td>
<td>0.46</td>
<td>129.87</td>
<td>0.9803</td>
<td>30.57</td>
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<tr>
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<td>212.77</td>
<td>0.9639</td>
<td>54.24</td>
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<td>0.8710</td>
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</table>
Based on the above models, the relative isotherm parameters for the adsorption of BPA at different temperatures were calculated and summarised in Table 8.2. The obtained correlation coefficient ($R^2$) values suggest that the adsorption of BPA by the organoclays intercalated with longer chain surfactants (HDTMA and DDDMA) were better fitted into the Langmuir isotherm model than the Freundlich isotherm while the Freundlich isotherm fitted the adsorption data for the organoclays intercalated with DDTMA at the lower temperature better. Higher values of $q_m$ were generally observed at the lower temperature which indicates that the adsorption is more favourable at the lower temperature.

### 8.3.4 Adsorption thermodynamics

The adsorbed amounts of BPA by the organoclays were measured in a range of temperatures 296.15 – 318.15 K, and the thermodynamic data obtained provides more in-depth information about the changes of internal energy that are associated with the adsorption of BPA. Details of the equations used for these calculations of the thermodynamic parameters are presented as below.

The distribution adsorption coefficient $K_d$ was calculated as follows,

$$K_d = \frac{C_0 - C_e}{C_e} \cdot \frac{V}{m} = \frac{q_e}{C_e}$$  \hspace{1cm} \text{Equation 8–1}

where $C_0$ and $C_e$ is the initial concentration and equilibrium concentration of the solute (mg/L), $V$ is the volume of the suspension (mg/L), $m$ is the mass of the adsorbent (g).

The equilibrium adsorption constant, $K^\circ$ was obtained from the plot between $\ln K_d$ and $C_e$ and the intercept of the plot gives the value of $\ln K^\circ$ which enables to calculate the standard free energy change, $\Delta G^\circ$.

$$\Delta G^\circ = -RT \ln K^\circ$$  \hspace{1cm} \text{Equation 8–2}

where $R$ is the universal gas constant (8.314 J/mol·K), $T$ is the absolute temperature (K)

The standard enthalpy and entropy changes, $\Delta H^\circ$ and $\Delta S^\circ$ can be calculated from the following equation
Table 8.3 Thermodynamics parameters for the adsorption of BPA by the organoclays

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp (K)</th>
<th>$lnK$</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/mol·K)</th>
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![Figure 8.4 Effect of the initial pH on the adsorption of BPA by MMT and organoclays](image-url)

Figure 8.4 Effect of the initial pH on the adsorption of BPA by MMT and organoclays

204
\[
\ln K^\circ = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}
\]

Equation 8 – 3

A plot of \(\ln K^\circ\) versus \(1/T\) gives a straight line and the slope and intercept of the plot are \(-\Delta H^\circ/R\) and \(\Delta S^\circ/R\), respectively.

The obtained parameters including the standard free energy (\(\Delta G^\circ\)), the standard enthalpy change (\(\Delta H^\circ\)), and the standard entropy change (\(\Delta S^\circ\)) are summarised in Table 8.3. The enthalpy changes obtained are negative and this suggests that the adsorption of BPA is an exothermic process; this also supports the observed decrease in the adsorption capacity of BPA with increasing temperature. In particular, the value of the adsorption enthalpy of BPA by the organoclays prepared with a 2.0 CEC became more negative than those prepared at 1.0 CEC, and this implied that the organoclays intercalated with higher surfactant loadings interacted with BPA more strongly. The negative change in free energy (\(\Delta G^\circ\)) observed showed that the adsorption was a spontaneous process. It is also noteworthy that the value of free energy became more negative with decreasing temperature. This indicates that the adsorption of BPA by organoclays is a more favourable and spontaneous process at a lower temperature. The negative \(\Delta S^\circ\) values suggest a decrease in randomness or disorder at the solid-liquid interface during the adsorption of BPA by the organoclays, while the negative values of \(\Delta S^\circ\) and \(\Delta H^\circ\) indicate that the adsorption process is more spontaneous at lower temperatures.

8.3.5 Effect of pH

The pH of the reaction mixture is one of the important factors that determines the adsorption properties of an adsorbent and the optimum condition for the adsorption process. The obtained result in Figure 8.4 showed the change in the amount of adsorbed BPA by MMT and organoclays with the initial pH ranging from 3 to 11. It was clearly seen that under acidic pH conditions the adsorption of BPA showed little change and remained fairly constant. When the pH rose beyond around 7, the adsorption of BPA gradually declined and even sharply decreased. These trends can be explained by the surface charge of the clays and the degree of dissociation of BPA solution at different pH values [6, 16, 34].

The siloxane (Si-O) group in the tetrahedral sheets on the external structure of MMT becomes Si-O', which is further converted into Si-OH at the different pH
Figure 8.5 Schematic diagram of the mechanism for the adsorption of BPA onto organoclays
environments employed. At an alkaline pH, the surface group is fully or partially deprotonated and this increases the negative charges on the surface of the clays. MMT was always negatively charged over the whole range of pH scales, as shown in the zeta potential from some studies [40, 41]. However, BPA remains as a neutral molecule when the pH of the solution goes below its pKa (i.e. pH < pKa) and prevailed as phenolate anions when the pH goes beyond the pKa (pH > pKa). In the current study, BPA has its molecular structure when pH < 7, and starts to deprotonate at around pH 8 with a second deprotonation form at the pH 10. A similar result was observed in the previous studies by Xu et al. [16] and Dong et al. [6]. However, such an explanation tends to overlook the fact that BPA ionises to mono- and divalent anions. Thus, the decreased adsorption of BPA in alkaline might be explained by the repulsive electrostatic interactions which occurred between the negatively charged surface of the clays and the bi-phenolate anions. It is also found that the organoclays with higher surfactant loadings and those prepared with larger surfactant molecules (e.g. DDDMA) were less influenced by the pH of the environment and consistently attracted anionic species of BPA even under the alkaline conditions.

8.3.6 Adsorption mechanism
The limited adsorption of BPA by the unmodified MMT was greatly improved when the MMT was converted to organoclays with organic surfactant molecules. It is clearly seen that the modified clays act as an effective adsorbents and the increase in the total organic carbon contents contributed to the increased hydrophobic lateral interactions. The loaded surfactants created the organic solvent-like hydrophobic phase and the interaction can be described as partition mechanism, resulting in a strong attraction of BPA molecules with the organoclays through Van der Waals interaction. It was found that the adsorption of the anion formed by BPA was greatly reduced under alkaline condition and that the main interaction expected between the BPA and the organoclays is the hydrophobic interaction (Figure 8.5a). In addition, there are several possible mechanisms for the adsorption of BPA, including electrostatic interaction, donor-acceptor complex formation, and hydrogen bonding.

The loaded organic surfactants tended to develop more positive charges on the clay surfaces by shielding the negative charge, which leads to greater attraction of the anionic forms of BPA. The dissociated BPA anions tended to associate with the positively charged head of surfactants on both inner and outer layer of the clays via
electrostatic interaction (Figure 8.5b). Another mechanism suggested in this adsorption system may be donor-acceptor complex formation between the solute and adsorbent. Although this is less energetic, as an electron acceptor, the positively charged head group of the surfactants interacted with the oxygen atoms of a phenol group in neutral BPA which acts an electron donator [6]. Hydrogen bonding was a potential mechanism suggested between the phenol groups of BPA and Si-O on clay surfaces. However, this binding may not contribute significantly to the adsorption of BPA by the unmodified MMT since less adsorption occurred. Thus, several possible mechanisms are proposed in this study, and the most likely mechanism appears to be a partitioning process into the hydrophobic phase created by the surfactant through Van der Waals and hydrophobic interaction.

8.3.7 Comparison the results with those obtained by other methods

Once the batch experiments were concluded, the optimised conditions and the mechanisms associated with the adsorption of BPA by the organoclays were determined. It was evident from the results that the adsorption by the organoclays is an effective method for the removal of BPA from aqueous medium. Although the obtained results cannot be directly compared with those obtained by the use other carbonaceous adsorbents such as graphene and zeolites, it appears that the adsorption by the organoclays offers a good pathway for the removal of BPA at ppm levels from water. In particular, the organoclays intercalated with the larger size of surfactants, DDDMA, are effective adsorbents for BPA. The prepared organoclays afforded 256.41 mg/g, which was the maximum adsorption values obtained from the Langmuir model at 302.15 K compared with values of 181.6 and 114.9 mg/g by graphene and zeolites reported in the previous study, respectively. Additionally, the uptake of BPA by the organoclays was little affected by varied pH environments up to pH 9.

Proceeding from obtained results, an optimum adsorption parameter was achieved when the pH of the solution is 8 and the use of organoclays is in the adsorption technique can be advantageous over the use of graphene. However, under the alkaline conditions, better adsorption of BPA by the zeolites was achieved. While the adsorption of BPA by the organoclays and graphene occurred over a similar time
scale, given the relatively low cost of production of the organoclays they may offer significant advantages in the removal of industrial pollutants from the environment [42]. The fate of the organoclays loaded with the adsorbed organic contaminants (e.g. BPA) will require further monitoring and investigations of the possible re-use of the adsorbents will be necessary in order to fully assess the practical implications of results described in this paper.

8.4 Conclusions
The investigation showed that the organoclays were found to be effective adsorbents for the removal of BPA from aqueous solutions. The adsorption of BPA was relatively influenced by pH and temperature. The adsorption of BPA was relatively decreased when the pH rose beyond 7 and the phenomenon can be explained due to the surface charge of the clays and the degree of dissociation of BPA solution. The organoclays intercalated with highly loaded surfactants and/or large surfactant molecules tended to be less influenced by the pH and this was due to the development of positive charges on the clay surface from surfactant molecules. The loaded surfactants acted as a partitioning phase and strongly attract to BPA molecules through hydrophobic interaction. The adsorption process occurred spontaneously and exothermic reaction was involved. The described results would support the use of organoclays as potential adsorbents for the removal of BPA from aqueous solutions.

Acknowledgement
The authors gratefully acknowledge and express gratitude for the financial and infrastructural assistance provided by Queensland University of Technology (QUT). The Australian Research Council (ARC) is thanked for funding some of the instrumentation.
8.5 References


CHAPTER 9
APPLICATION OF ORGANOCLAYS FOR
THE ADSORPTION OF HERBICIDES AND
PESTICIDES

This paper will be submitted for publication:

PREFACE

The high adsorption capacities of the organoclays for the uptake of BPA observed in the previous paper and demonstrated their potential application as strong adsorbents for noxious organic water contaminants. As shown in the paper, the adsorption of BPA was significantly influenced by pH, with increased adsorption occurring in acidic environments. In particular, the organoclays intercalated with large organic cations and/or high saturations of surfactants were less influenced by the pH of the environment. The paper in Chapter 8 thus clearly described a potential pathway for the removal of BPA from contaminated waters.

Chapter 9 demonstrated the adsorption of agricultural pollutants such as imazaquin and atrazine from aqueous solutions. The paper examined the optimum conditions as well as the mechanisms involved in the adsorption of these herbicides using organoclays intercalated with HDTMA, DDTMA, and DDDMA and compared the adsorption of herbicides. It further investigated the adsorption of a mixture containing imazaquin and atrazine in order to determine their comparative adsorption rates. The result indicated that given the potential utility of the organoclays, they can be considered as suitable materials for the removal of persistent herbicides.
STATEMENT OF CONTRIBUTION OF CO-AUTHORS

The authors listed below have certified* that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
3. there are no other authors of the publication according to these criteria;
4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and
5. they agree to the use of the publication in the student’s thesis and its publication on the QUT ePrints database consistent with any limitations set by publisher requirements.

In the case of this chapter:

Removal of herbicides from aqueous solutions by modified forms of montmorillonite.
Accepted for publication in Journal of Colloid and Interface Science on 15th Oct 2013.

<table>
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<th>Contributor</th>
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<tr>
<td>Yuri Park (candidate)</td>
<td>Developed experimental design, conducted experiments, analysed data, and wrote the manuscript.</td>
</tr>
<tr>
<td>Zhiming Sun</td>
<td>Conducted experiments and analysed analysis</td>
</tr>
<tr>
<td>Godwin A. Ayoko* (Principal Supervisor)</td>
<td>Assisted in the experimental design, data analysis and edited the manuscript.</td>
</tr>
<tr>
<td>Ray L. Frost (Associate Supervisor)</td>
<td>Assisted in the experimental design, data analysis and edited the manuscript.</td>
</tr>
</tbody>
</table>

Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

[Signature]

Name  Signature  Date

15/10/2013
9.1 Introduction

The security of surface and groundwater from pollution is a growing concern in many areas of the world [1]. A lot of attention has been paid to environmental problems associated with the presence of contaminants, including inorganic (e.g. heavy metals) and organic compounds (e.g. herbicides and pesticide, and polycyclic aromatic hydrocarbons (PAHs)) derived from agricultural and industrial activities in water. In the agricultural industry, atrazine is a type of triazine herbicide that is widely used as a plant-protecting agent [2-4], while imazaquin is an imidazolinone class herbicide that is designed to control weeds in soybeans [5-7] (see Figure 9.1). The use of the agrochemicals to control organisms is a current concern as they dissolve in the soil and exacerbate the risk associated with runoff to surface and groundwater [8-12]. Hence, the attention researchers have been drawn to these public health and environmental concerns and the need to improve the quality of groundwater, especially, in areas where the loading of these compounds occurs [13].

![Chemical structure of imazaquin and atrazine](image)

<table>
<thead>
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<th></th>
<th>Imazaquin</th>
<th>Atrazine</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Log K\text{ow}^1</strong></td>
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<td>2.68</td>
</tr>
<tr>
<td><strong>Solubility</strong></td>
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<td>33 mg/L at 25 ºC</td>
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</table>

1 Octanol-water partition coefficients

**Figure 9.1 Molecular structures and properties of herbicides (a) imazaquin and (b) atrazine**

To resolve this issue, many studies have been conducted to develop inexpensive, effective and efficient methods to remediate water from pollution without producing secondary pollutants by the treatment [13]. One treatment technique suggested in this
study is the adsorption process, which has relatively lower operational cost, ease of operation and low tendency for the production of toxic secondary products [14].

Clay minerals and modified clay minerals are good candidate adsorbents for the remediation of environmental contaminants due to their unique features [15]. Clay minerals are abundant in nature, and possess layered structure and ion exchange properties, which enhance the modification of their surfaces with organic cations in order to increase their affinity for organic pollutants [16-19]. Replacement of inorganic exchangeable cations (Na\(^+\) or Ca\(^{2+}\)) with organic cations yields hydrophobic organoclays and this simple modification is widely used to improve the adsorptive capacity of clays for hydrophobic organic compounds. Quaternary ammonium cations (QACs) are one of the commonly used organic cations for such modifications and many previous studies have investigated in the development of modified clays with non functionalised QACs or functionalised QACs for the adsorption of organic compounds [19-22]. Results from these studies indicate that the selection of the organic cations is critical to the performance of organoclays for the removal of organic pollutants.

Hence, in this research, the potential use of organoclays as adsorbents was investigated for the removal of two different forms of herbicides; imazaquin and atrazine. The preparation of organoclays was initially conducted by (i) the use of different types of non functionalised QACs at different concentrations of the surfactants, and (ii) investigation and comparison of the adsorptive properties of three different organoclays, dodecyltrimethylammonium-, hexadecyltrimethylammonium-, and didodecyltrimethylammonium- exchanged montmorillonites. The objective of this work was to determine the optimal conditions for the removal of the herbicides from water under different conditions (e.g. agitation time, pH, and different concentrations of herbicides) and evaluate the mechanisms involved in the adsorption process of herbicides.

9.2 Experimental methods

9.2.1 Materials
Pure Na-montmorillonite (referred as MMT) was purchased from Sigma-Aldrich and was used without purification. Based on the product specification, its cation exchange capacity (CEC) is 76.4 meq/100g. Three different types of cationic
surfactants were purchased from Sigma-Aldrich: (i) dodecyltrimethylammonium bromide (denoted as DDTMA, C\textsubscript{15}H\textsubscript{34}NBr, FW:308.34), (ii) hexadecyltrimethylammonium bromide (denoted as HDTMA, C\textsubscript{19}H\textsubscript{42}NBr, FW:364.46), and didodecyldimethylammonium bromide (denoted as DDDMA, C\textsubscript{26}H\textsubscript{56}NBr, FW:462.65).

9.2.2 Synthesis and characterisation of organoclays

The organoclays prepared are described in detail in a previously published paper by Park et al.\cite{23,24} and were characterised by various techniques including X-ray diffraction (XRD), surface area measurement (BET method), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA). Their structural properties and characteristics were described by the previous work\cite{23,24}.

9.2.3 Batch adsorption of herbicides

Two different types of herbicides, imazaquin (2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinoline-carboxylic acid) and atrazine (6-chloro-N-ethyl-N-(1-methylethyl)-1,3,5-triazine-2,4-diamine) were purchased from Sigma-Aldrich. Both imazaquin and atrazine were initially prepared in methanol as a stock solution (100 mg/L) and further diluted in water for the appropriate concentrations (0.5 – 20 mg/L). 0.1 – 0.2 g of the organoclays were placed in sealed 50 mL centrifuge tubes with 40 mL of imazaquin and/or atrazine solution in the appropriate concentration. The tubes were placed in a rotary shaker or a shaking water bath for 12 hr at the appropriate temperature at 25 and 35 °C. The initial pH of imazaquin and atrazine was about pH 5 and 5.5. The mixture was filtered through PTFE 0.22 µm filters and the supernatants were analyzed by a UV-Vis spectrometer (Agilent Cary 50) at 240 and 220 nm for imazaquin and atrazine, respectively, and a high-performance liquid chromatography (HPLC, Agilent HP 1100). The following conditions for the HPLC were used: 60:40 Acetonitrile/water eluent mixture at a flow rate of 1 mL/min, a Luna 5 µ C18 column (Phenomenex Pty Ltd), 100 µL injection volume, and UV detection at 240 and 220 nm, respectively. To conduct the kinetic study (from 10 to 240 min), the adsorbents were added with an initial herbicides concentration (5 mg/L) at room temperature in determination of the equilibrium concentration. To evaluate the effect of pH on the adsorption of BPA (5 mg/L as an initial concentration of herbicides), the final pH of herbicides solutions
were adjusted by either diluted 0.1 M HCl or NaOH. The quantity \((q_e)\) of the adsorbed solutions was calculated [23, 24].

9.3 Results and discussion

9.3.1 Adsorption of imazaquin and atrazine from single-component solutions

The fully characterised organoclays were used to evaluate their adsorption capacities for the removal of imazaquin and atrazine from aqueous solutions. Generally, the low adsorption of the herbicides onto hydrophilic MMT was observed and the adsorption results (in Figure 9.2) demonstrated that the organoclays can remove 93.1 and 47.1 % of imazaquin and atrazine, respectively.

![Figure 9.2](image-url)
<table>
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<th>Sample</th>
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<th>Pseudo-second order</th>
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<tr>
<td>1.0 CEC-DDTMA</td>
<td>0.0032</td>
<td>20.876</td>
<td>0.3833</td>
<td>0.8057</td>
</tr>
<tr>
<td>1.0 CEC-HDTMA</td>
<td>0.0042</td>
<td>5.5212</td>
<td>0.6896</td>
<td>0.2284</td>
</tr>
<tr>
<td>1.0 CEC-DDDMA</td>
<td>0.0038</td>
<td>4.9441</td>
<td>0.6407</td>
<td>0.2400</td>
</tr>
</tbody>
</table>

Figure 9.3 Effect of agitation time for the adsorption of imazaquin (a) and atrazine (b)
It was found that organoclays were highly effective for the removal of imazaquin, but their efficiency in the adsorption of atrazine was relatively low. The results also showed that the amount of adsorbed herbicides was influenced by the size of surfactants as well as the saturation of organic cations. A similar finding from the investigation [25] reported the importance of the organic cations. Introduction of larger organic cations into the interlayer space of MMT has been attributed to an increase in basal spacing, which resulted in higher adsorption of herbicides. This study also demonstrated the packing density with an increase of surfactant loadings affected the adsorption of herbicides, but this factor may not be significantly affected in the current study.

Given the initial adsorption by organoclays intercalated with the different types of surfactants, the kinetic study of herbicide adsorption using organoclays was conducted (see Figure 9.3). It appears that the amounts of imazaquin and atrazine adsorbed by the organoclays rose slightly in the first 80 min and reached an equilibrium concentration within 2 hr, indicating a slow adsorption process compared with the previous study for the removal of phenolic compounds [23, 24].

To explain the adsorption process in detail, two conventional kinetic models, pseudo-first order and pseudo-second order models were applied to the experimental data. The obtained data is summarised in Table 9.1.

The pseudo-second order model fitted better than the pseudo-first order model in this study as illustrated by the high correlation coefficient \(R^2\) values obtained in the adsorption of both imazaquin and atrazine. The parameter, \(k_2\), which shows the reaction rate during the adsorption process, indicates that the adsorption of herbicides by the organoclays intercalated with smaller organic cations tended to reach the equilibrium concentration quicker than those intercalated with larger organic cations. This can be attributed to the different pore sizes of the modified clays obtained with the different size of organic cations [23]. The loaded surfactant molecules blocked the pores and the sizes of pores became smaller, while the adsorption of the herbicides onto the organoclays slowed down. The observed pseudo-second order model in the adsorption of herbicides showed that the chemical reaction was significantly controlled in the rate controlling step.
Table 9.2 Langmuir and Freundlich isotherm models

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_L$ (L/mg)</td>
<td>$q_m$ (mg/g)</td>
</tr>
<tr>
<td><strong>Imazaquin</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 CEC-DDTMA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>0.1653</td>
<td>0.0963</td>
</tr>
<tr>
<td>35</td>
<td>0.6488</td>
<td>0.2369</td>
</tr>
<tr>
<td>1.0 CEC-HDTMA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>0.5844</td>
<td>1.7180</td>
</tr>
<tr>
<td>35</td>
<td>1.4544</td>
<td>5.7143</td>
</tr>
<tr>
<td>1.0 CEC-DDDMA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>0.5117</td>
<td>3.6324</td>
</tr>
<tr>
<td>35</td>
<td>1.6268</td>
<td>10.977</td>
</tr>
<tr>
<td><strong>Atrazine</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 CEC-DDTMA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>0.0419</td>
<td>0.5811</td>
</tr>
<tr>
<td>35</td>
<td>0.0543</td>
<td>0.3388</td>
</tr>
<tr>
<td>1.0 CEC-HDTMA</td>
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<td></td>
</tr>
<tr>
<td>23</td>
<td>0.0288</td>
<td>2.6082</td>
</tr>
<tr>
<td>35</td>
<td>0.1088</td>
<td>0.0846</td>
</tr>
<tr>
<td>1.0 CEC-DDDMA</td>
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<td></td>
</tr>
<tr>
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<td>1.5836</td>
</tr>
<tr>
<td>35</td>
<td>0.0792</td>
<td>1.1101</td>
</tr>
</tbody>
</table>

Figure 9.4 Effect of pH on the adsorption of herbicides by organoclays
Several adsorption isotherm models were applied to describe the adsorption of the herbicides by the organoclays and Table 9.2 summarises the parameters obtained for the Langmuir and Freundlich isotherm models. With the exception of 1.0 CEC-DDTMA, the adsorption of imazaquin fitted the Freundlich isotherm model best, while the higher correlation coefficient values ($R^2 > 0.91$) in the adsorption of atrazine showed that it followed the Langmuir isotherm model. The obtained $K_L$ and $K_F$ values from the isotherm models indicated that the adsorption capacities of organoclays for both imazaquin and atrazine are high. This was clearly evident by the Freundlich $K_F$ and Langmuir $K_L$ values for the organoclays. The adsorption of imazaquin by the organoclays tended to increase when the temperature increased from 25 to 35 ºC and this is ascribed to the high affinity of the herbicide for the organoclays at higher temperatures. However, the higher adsorption of atrazine was shown at lower temperatures.

According to Weber, herbicides are highly influenced by pH change and can be formed either as protonated or neutral species [26]. Therefore, this investigation attempted to describe the adsorption properties of organoclays for the removal of imazaquin and atrazine at varied pH environments from pH 2 to 7.

Figure 9.4 shows that the adsorption of atrazine was little affected by the investigated pH conditions ranging from pH 2 to 7. However, changes in the pH conditions affected the amount of adsorbed imazaquin. In particular, different adsorption properties towards imazaquin were shown by the organoclays intercalated with different sizes of organic cations. For example, the adsorption of imazaquin by the organoclays intercalated with DDTMA decreased gradually while the adsorption by those intercalated with HDTMA and DDDMA improved slightly and gradually declined above pH 5. These observations attributed to the size of organic cations and the properties of the herbicide molecules. Imazaquin has an amphoteric structure with an acidic carboxylic acid group and a basic quinoline functional group at $pK_a$ values of 3.8 and 2.0, respectively [27]. Thus, imazaquin exists in the anionic form when the pH is lower than 5. When the pH decreases, the anionic form of imazaquin becomes neutral due to the protonation of the carboxylic acid group (-COOH), resulting in a loss of negative charge. However, when the pH further declines, the neutral molecule gains a positive charge from the protonation of the quinoline group, and cationic imazaquin forms at lower pH.
Figure 9.5 The amounts of adsorbed herbicides onto organoclays from single and mixed component solutions

Table 9.3 Percentage of removal herbicides from a comparative adsorption

<table>
<thead>
<tr>
<th>Sample</th>
<th>Imazaquin</th>
<th>Atrazine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial conc.</td>
<td>% Removal$^1$</td>
</tr>
<tr>
<td>1.0 CEC-DDTMA</td>
<td>10</td>
<td>1.914</td>
</tr>
<tr>
<td>2.0 CEC-DDTMA</td>
<td>10</td>
<td>4.385</td>
</tr>
<tr>
<td>1.0 CEC-HDTMA</td>
<td>10</td>
<td>62.77</td>
</tr>
<tr>
<td>2.0 CEC-HDTMA</td>
<td>10</td>
<td>90.47</td>
</tr>
<tr>
<td>1.0 CEC-DDDMA</td>
<td>10</td>
<td>67.61</td>
</tr>
<tr>
<td>1.5 CEC-DDDMA</td>
<td>10</td>
<td>90.32</td>
</tr>
</tbody>
</table>

$^1$ is the quantity of adsorbed herbicides from single component solutions

$^2$ is the quantity of adsorbed herbicides from mixed component solutions
The loaded larger surfactants (DDDMA) tended to develop more positive charges within the MMT and attract the anionic form of imazaquin at the lower pH through electrostatic interactions. By shielding the negatively charged clay surface of MMT with cationic surfactant molecules, high adsorption was observed [5]. At the lower pH, the neutral imazaquin might interact with the organoclays via hydrophobic interaction. In this regard, the observation of little adsorption of atrazine due to the fact that the atrazine becomes protonated and it is present in the cationic form when the pH is lower [3]. According to Tao and Tang [2], maximum adsorption of atrazine occurred at pH close to its pKₐ (1.68), when cationic and neutral species of atrazine are present equally. Their result has been reflected in this study by the observation that the atrazine was not likely protonated at the investigated pH conditions so that only the neutral type of atrazine was adsorbed by the organoclays, and the interaction could involve van der Waals forces.

9.3.2 Adsorption of herbicides from mixed solutions
This study also investigated a comparative adsorption of the mixture of imazaquin and atrazine by the organoclays intercalated with the long chain surfactants, with the percentages of the imazaquin and atrazine removed presented in Figure 9.5 and Table 9.3. The table shows that the adsorption of the two herbicides in the mixture was slightly enhanced compared with the adsorption of imazaquin and atrazine in solutions containing each of the herbicides. In particular, the adsorption of atrazine was greatly improved in keeping with the results from a previous study [28]. According to Undabeytia et al., this observation was due to a synergistic effect. It was suggested that the effect is due to the different hydrophobic properties of imazaquin and atrazine, and the partitioning of imazaquin in the interlayer space, resulting in the decrease of interfacial tension, which supports the greater affinity for atrazine [28].

9.3.3 Mechanism for the adsorption of herbicides
The investigation showed that negligible amounts of herbicides (imazaquin and atrazine) were adsorbed by MMT, and they were greatly improved by the modification of the clays with surfactants. It is evident that the organoclays are better
adsorbents for the removal of herbicides. In particular, different adsorption capacities of organoclays towards the imazaquin and atrazine were observed and this is likely due to the degree of organic cation saturations, the size of organic cations and the different natures of the herbicides used in this study.

Both imazaquin and atrazine displayed a great affinity for the organoclays with longer chain surfactants (e.g. HDTMA and DDDMA) and also those prepared at high concentrations of surfactants. The loaded organic surfactants have a tendency to develop more positive charges on the surface of MMT by shielding the negative charge, resulting in increased attraction of the anionic forms of the herbicide.

The amphoteric imazaquin is highly affected by the changes of pH. In pH range 5 – 7, the anionic imazaquin becomes a neutral species and then a cationic species form when the pH declines. Similarly, a neutral atrazine exists as a cation at low pH (lower than 1.68 of pKa). Thus, one of the factors regulating the sorption of neutral forms of imazaquin and atrazine for the organoclays can be a hydrophobic interaction. Another mechanism that can dictate the sorption of herbicides is the electrostatic interaction. There is probably a high interaction between the anionic imazaquin and the organic cations on the external surfaces of the organoclays, leading to the higher sorption potential for the imazaquin than for the weakly basic atrazine in this study. Thus, electrostatic interaction is the primary sorption mechanism involved. In addition, the lower adsorption of atrazine by the organoclays can be due to the different hydrophobic properties and the presence of the large aromaticity in the structure of atrazine may thwart the close approaches to organoclays [28].

The adsorption of imazaquin and atrazine is influenced by temperature with higher adsorption affinity of herbicides for organoclays being observed for increased temperatures. The adsorption of imazaquin and atrazine followed Langmuir and Freundlich isotherm models, respectively, indicating different adsorption properties of the organoclays for the removal of herbicides from the aqueous solutions.
9.4 Conclusions

The modification of MMT with organic cations is found to be a potentially important technique for the removal of recalcitrant herbicides from contaminated water. In particular, imazaquin displayed very strong affinities for the organoclays intercalated with longer organic cations (e.g. HDTMA and DDDMA) at the higher surfactant concentrations through electrostatic and hydrophobic interactions. In contrast, organoclays are not potentially good adsorbents for the removal of atrazine but the adsorption of atrazine is greatly improved when the mixture containing both imazaquin and atrazine. This phenomenon is described as a synergetic effect. The enhancement and full understanding of the adsorption process will require further investigation under varied environmental factors.

Acknowledgement

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9.5 References


CHAPTER 10
GENERAL CONCLUSIONS AND
RECOMMENDATIONS FOR FUTURE WORK
10.1 Conclusions

The literature review has shown that there is a strong tendency to use clay minerals as adsorbents for environmental remediation. Clay minerals are hydrophilic and their use remains limited for the removal of organic contaminants. The surface properties have, however, been modified by replacing exchangeable cations (Na\(^+\) or Ca\(^{2+}\)) with QACs through ion exchange. The modified clay minerals become hydrophobic/lipophilic organoclays, and have significantly improved abilities to remove organic contaminants that are found in surface and ground water.

Recent studies have reported the effectiveness of organoclays for the uptake of organic contaminants, including aromatic organic compounds, phenolic compounds, and pesticides/herbicides. Meanwhile, many studies have suggested a number of important factors that affect the adsorption capacity of organoclays, including temperature, pH, and different concentrations of pollutants. Considering all the literature reviews, the potential of organoclays for the removal of emerging pollutants such as hormones, pharmaceutical and personal care products (PPCPs) from aqueous solutions needs to be explored. Therefore, this thesis has increased our fundamental knowledge of the synthesis and characteristics properties as well as the potential of organoclays as adsorbents for the removal of organic pollutants. The thesis included three different research themes, all with the purpose of better describing the outcomes associated with the objectives of the overall project.

In the thesis, the typical 2:1 layered montmorillonite, consisting of two siloxane tetrahedral sheets with an aluminium octahedral sheet was initially modified with long chain alkyl cationic surfactants (HDTMA, DDTMA, DDDMA and TDTMA) at different concentrations. The loadings of the different concentrations of surfactants led to the different degrees of interlayer spacings in the organoclays. The different expansions in the interlayer space of the organoclays observed were due to the different arrangements of surfactants within the layers. For example, at lower concentrations of surfactants (<1.0 CEC loading), an expansion was shown and a simple monolayer or bilayer type of arrangement was formed. Above 1.0 CEC, the configuration of pseudo-trimolecular layer structures formed. However, the pseudo-trimolecular structure was not formed in the organoclays intercalated with DDTMA. From the XRD pattern and respective basal spacings, changes of surfactant arrangements were found as a function of surfactant concentration. In particular, the
interlayer spacing of the organoclays intercalated with DDDMA increased significantly and paraffin type layers were only observed when DDDMA was loaded.

The thesis analysed the structural and configurational changes in different types of organoclays and determined the thermal stabilities of the organoclays by TG. In general, there are four steps observed: (i) dehydration of water, (ii) dehydration/dehydroxylation of water near metal cations, (iii) decomposition of surfactant, and (iv) dehydroxylation of structural OH units in the clays. In the desurfactant process of the organoclays intercalated with TDTMA, there was a single peak at the lower surfactant loadings (0.25 and 0.5 CEC) and a new peak appeared in the region with an increase of surfactant loading (1.0 – 2.0 CEC). This was due to the interactions of loaded surfactants at different sites, either in the interlayer space or on the external surfaces of MMT. The loaded surfactants in the interlayer space strongly adhered electrostatically and resulted in an increase in decomposition temperature. The decomposition temperature of surfactants which was attached on the external surface of MMT, became lower and was close to that of pure surfactant. The thermal stability of the organoclays was found to be more significant at lower surfactant concentrations. Thus, the use of TG enabled the calculation of the actual mass of organic molecules present in organoclays, and the data from DDTMA-MMT and DDDMA-MMT showed that the obtained results were highly correlated with the basal spacings observed in the XRD analyses. The amount of DDTMA increased up to 1.0 CEC and remained constant above 1.0. The actual loading of DDDMA kept increasing as the function of surfactant concentration. XRD and TG provided the structural properties of organoclays and showed that organoclays became more hydrophobic as a function of surfactant loading as well as the size of surfactants.

To support and probe the molecular structures of the intercalated surfactants within the organoclays, infrared spectroscopy is necessary. The infrared spectra of organoclays intercalated with HDTMA, DDTMA, DDDMA and TDTMA showed that as the surfactant loading reached 1.0 CEC, water molecules in MMT were gradually displaced with the loaded surfactants in the interlayer space. Hence, the internal surface of clays became more hydrophobic. The wavenumber of CH stretching peaks from surfactant molecules shifted significantly as the surfactant loadings increased. It was found that CH mode was highly sensitive to the
conformational changes of the surfactants in the organoclays and this mode could be qualitatively monitored.

The thesis has also identified the porosity and structural parameters of MMT and modified clays with surfactants (HDTMA, DDTMA, DDDMA and TDTMA). The organoclays all formed a type II sorption behaviour, indicating a multiple adsorption and the presence of mesopores. Decreased BET surface area and pore volume for organoclays were observed with an increase in surfactant loadings. It showed that the packing density of organoclays constantly increased and the loaded surfactant played an important function in the distribution of the structure of organoclays.

The surface chemical composition of organoclays intercalated with four different surfactants was analysed using XPS and binding energies from high resolution XPS results, provided information on the changes in the structures of organoclays. Upon increasing the surfactant loading, increased ratios of C/Si and C-C bond were obtained, while the C-N bond remained constant. By contrast, the binding energy in the ratio of Si/Al decreased. The changes were associated with the changes of surfactant arrangements and the loaded surfactants caused alterations in the distance between Al-O(OH) octahedral sheets and the two Si-O tetrahedral sheets in the structure of MMT.

Attempts have been made to simulate the conformational changes of surfactant molecules (HDTMA, DDTMA and DDDMA) within organoclays using MM calculation. For example, the surfactant HDTMA was presented as a monolayer at lower surfactant concentrations (e.g. 0.5 CEC) and became a double-layer type structure (e.g. 1.0 CEC) at increased concentrations. As the surfactant loading further increased (e.g. 2.0 CEC), pseudo-trimolecular type (head-to-tail-to-head pattern) were observed. Similarly, the MM calculation confirmed that DDTMA presented as a monolayer type (e.g. 0.5 CEC) and a double layer type (e.g. 1.0 CEC). The structural variations of DDDMA in the interlayer space were described as a monolayer type at lower HDTMA loadings (e.g. 0.25 CEC). When the surfactant loading increased at 1.0 CEC a double-layer type was observed and above 1.0 CEC, a mixed structure with an alternative pattern was described. The proposed conformational changes of surfactant molecules showed that the system energy of the basal spacing and the models fitted with the experimental results.
The thesis has further identified the potential of organoclays intercalated with HDTMA, DDTMA and DDDMA for the removal of organic water pollutants, including phenolic compounds (e.g. PCP and PNP), emerging pollutants (e.g. BPA) and herbicides/pesticides (e.g. imazaquin and atrazine). It has been found that the removal of 44 and 4.8 % for PNP and PCP by MMT was improved up to 89.1 and 67.0 % and further to 98.2 and 86.0 % by organoclays intercalated with HDTMA at 1.0 and 2.0 CEC, respectively. On the other hand, the organoclays intercalated with DDDMA adsorbed 99.5 and 94.9 % for PNP and PCP, respectively.

Taking into consideration the fact that the amount of adsorbed BPA removed by MMT was 6.3 %, and the adsorption of BPA was 96.3 and 98.9 % by the organoclays intercalated with DDTMA and HDTMA at 1.0 CEC, the potential of the organoclays as viable adsorbents for BPA was demonstrated. In particular, the organoclays intercalated with DDDMA adsorbed 99.5 % of BPA at 1.0 CEC. The results confirmed that the adsorption of BPA by organoclays, especially, the organoclays intercalated with DDDMA were highly effective.

The organoclays were tested for the removal of imazaquin and atrazine. The negligible amount of adsorbed imazaquin and atrazine by MMT was improved up to 80.3 and 25.0 % by the organoclays intercalated with HDTMA at 1.0 CEC. The amount of adsorbed imazaquin and atrazine by organoclays intercalated with DDDMA was increased to 89.0 and 40.0 % at 1.0 CEC. In comparison with results for the adsorption of herbicides, the removal of atrazine using organoclays has been found to be minimal.

With the percentage removal of different types of organic contaminants, the obtained results provided empirical evidence to substantiate the assumption that organoclays are potentially cost effective and efficient adsorbents for organic environmental pollutants in aqueous media. The organoclays favourably increased the adsorption capacity of organic contaminants and this was relatively influenced by the degree of organic surfactant saturations as well as the size of the surfactant molecules.

The thesis looked at the adsorption of organic contaminants at different experimental conditions in order to determine the optimum conditions and identify the mechanisms involved. The kinetic studies showed that with the exception of the herbicides, the adsorption of the organic compounds occurred spontaneously and
reached equilibrium concentrations within 1 hr. The adsorption of organic pollutants by organoclays tended to be lower when the temperature increased, indicating that the reactions were exothermic. However, the adsorption of herbicides was shown to be different as the amount of adsorbed imazaquin improved at higher temperatures. The thesis also showed that the adsorption of the organic compounds was highly dependent on the pH, and subject to the dissociation behaviour and nature of pollutants as well as the surface charge of the clays. The adsorption of organic contaminants at different concentrations of pollutant solutions led to the identification of the adsorption isotherm models (e.g. Langmuir and Freundlich isotherms) that best described the adsorption process. The adsorption of phenolic compounds (PNP and PCP) and atrazine best fitted into the Freundlich isotherm, while the Langmuir adsorption isotherm model was suggested for the adsorption of BPA and imazaquin.

Overall, the prepared organoclays have been examined for the removal of different classes of organic pollutants from aqueous solutions. Thus, the thesis has promoted the potential application of organoclays as adsorbents for environmental remediation, and, the studies reported in the thesis pointed to several promising applications of organoclays in future research.

10.2 Recommendations for future study

This research has greatly extended our understanding of synthesis and characteristic properties of organoclays as potential adsorbents for the removal of organic contaminants. It is suggested that further investigations into the adsorption of herbicides and pesticides, noted in this thesis for their lower performance, be undertaken with the aim to improve the adsorption of these pollutants by organoclays. This could involve the examination of surfactants with organic cations containing different functional groups.

In the synthesis of organoclays with organic molecules, non-toxic organic cation types would be considered for the further modification of clay minerals to be environmentally safe, and the efficiency of the materials and their potential applications will be further investigated.
Future studies also need to consider the leaching of surfactants and desorption of adsorbed pollutants, and to ensure that the use of organoclays is environmentally safe.

A comparative adsorption investigation could also be considered. In real practice, mixtures of various pollutants derived from the industry and environment present in water and adsorption studies on mixtures of pollutants by organoclays might mimic the situation in the real world better.

It is also worthwhile to investigate the methods of re-use of surfactant or re-generation of organoclays further. This investigation will reduce any environmental risks and lower the treatment cost in real industrial and environmental practice and hence, further investigations are suggested.

Finally, this research has demonstrated that the adsorption of organic water contaminants has been conducted by batch experiments at the laboratory scale. For this technique to be more applicable, the design and development of a small-scale pilot column should be considered for water purification in further studies.