SYNTHESIS OF MESOPOROUS MATERIALS AS ADSORBENT FOR ADSORPTION AND DESORPTION OF PARAQUAT

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Very special dedication to my beloved parents, Japri bin Khamis and Mayzurah binti Basri, my husband, Ahmad Uzair bin Said, respected supervisor, Assoc. Prof. Dr. Zainab binti Ramli, all lecturers, families and friends. Thank you for the prayers, supports and encouragements.

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ABSTRACT

Paraquat is a pesticide that is used to control weeds but it is very poisonous to humans and environment. Therefore, removal of paraquat from the environment is very important and in poisoning cases that involve paraquat, the sample need to be preconcentrated prior to analysis because the pesticide concentration may very low to be measured and in small sample size. In this research, several types of mesoporous materials were synthesised to adsorb and desorb paraquat namely mesoporous aluminosilicate using various saccharides templates as mesoporous directing agent which are glucose (MAS-GLU), lactose (MAS-LAC), sucrose (MAS-SUC) and without saccharide template (MAS-WOT) and being compared to mesoporous silica material, MCM-41. The formations of synthesised materials were confirmed from FTIR, XRD, SAXS, XRF and surface area analysis. The characterisation results revealed that MAS-SUC formed mesoporous aluminosilicate with ZSM-5 zeolite framework, MAS-GLU, MAS-LAC and MAS-WOT formed mesoporous aluminosilicate with amorphous structure and MCM-41 is mesoporous silica. MAS-SUC, MAS-WOT and MCM-41 were chosen as the representative of different type of mesoporous materials for adsorption and desorption experiment. From the adsorption result of paraquat, it showed that the maximum adsorption capacity in the order of MAS-WOT, MAS-SUC and MCM-41 with maximum adsorption capacity 37.59 mg/g, 36.76 mg/g and 4.45 mg/g respectively. The isotherm study shows all adsorbents fit Langmuir isotherm better than Freundlich isotherm. The desorption results revealed that desorption by sonication process is better than shaking process and even though MAS-WOT and MAS-SUC have good adsorption ability, but paraquat not able to desorb well from them. Only 33% of adsorbed paraquat can be desorbed from MAS-WOT and 31% from MAS-SUC. MCM-41 showed better desorption ability because almost 100% of the analyte able to be desorbed. Study showed that mesoporous aluminosilicate materials are better adsorbents as compared to MCM-41, but poor in desorption ability for paraquat.

ABSTRAK

Parakuat ialah racun perosak yang digunakan untuk mengawal rumpai tetapi ia sangat beracun kepada manusia dan alam sekitar. Oleh itu, penyingkiran parakuat dari alam sekitar adalah sangat penting dan dalam kes-kes keracunan yang melibatkan parakuat, sampel perlu diprakonsentrasi sebelum dianalisis kerana kepekatan racun perosak yang berkemungkinan sangat rendah untuk diukur dan saiz sampel yang kecil. Dalam kajian ini, beberapa jenis bahan mesoliang telah disintesis untuk menjerap dan menyahjerap parakuat iaitu mesoliang aluminosilikat menggunakan pelbagai templat sakarida sebagai ejen pengarahan mesoliang iaitu glukosa (MAS-GLU), laktosa (MAS-LAC), sukrosa (MAS-SUC) dan tanpa templat sakarida (MAS-WOT) dan dibandingkan dengan bahan mesoliang silika, MCM-41. Pembentukan bahan disintesis telah disahkan dari FTIR, XRD, SAXS, XRF dan analisis kawasan permukaan. Keputusan pencirian mendedahkan bahawa MAS-SUC membentuk mesoliang aluminosilikat dengan kerangka zeolit ZSM-5, MAS-GLU, MAS-LAC dan MAS-WOT membentuk mesoliang aluminosilikat dengan struktur amorfus dan MCM-41 adalah mesoliang silika. MAS-SUC, MAS-WOT dan MCM-41 telah dipilih sebagai wakil bahan mesoliang yang berlainan jenis untuk eksperimen penjerapan dan penyahjerapan. Dari hasil penjerapan parakuat, ia menunjukkan bahawa kapasiti penjerapan maksimum dalam urutan MAS-WOT, MAS-SUC dan MCM-41 dengan kapasiti penjerapan maksimum 37.59 mg/g, 36.76 mg/g dan 4.45 mg/g masing-masing. Kajian isoterma menunjukkan semua penjerap mematuhi isoterma Langmuir lebih baik daripada isoterma Freundlich. Keputusan penyahjerapan mendedahkan bahawa penyahjerapan oleh proses sonikasi adalah lebih baik daripada proses goncangan dan walaupun MAS-WOT dan MAS-SUC mempunyai keupayaan penjerapan yang baik, tetapi parakuat tidak dapat dinyahjerap dengan baik dari mereka. Hanya 33% daripada parakuat yang terjerap boleh dinyahjerap dari MAS-WOT dan 31% dari MAS-SUC. MCM-41 menunjukkan kebolehan penyahjerapan yang lebih baik kerana hampir 100% daripada analit dapat dinyahjerap. Kajian menunjukkan bahawa bahan-bahan mesoliang aluminosilikat adalah penjerap yang lebih baik berbanding dengan MCM-41, tetapi kurang keupayaan dalam penyahjerapan parakuat.

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LIST OF ABBREVIATIONS

λ_{max}	-	Maximum Absorption Wavelength
BSA	-	Bovine Serum Albumin
CE	-	Capillary Electrophoresis
CTABr	-	Cetyltrimethylammonium Bromide
FTIR	-	Fourier Transform Infrared Spectroscopy
IUPAC	-	International Union of Pure and Applied Chemistry
IZA	-	International Zeolite Association
MAA	-	Methacrylic Acid
MAS-GLU	-	Mesoporous aluminosilicate that synthesised with glucose template
MAS-LAC	-	Mesoporous aluminosilicate that synthesised with lactose template
MAS-SUC	-	Mesoporous aluminosilicate that synthesised with sucrose template
MAS-WOT	-	Mesoporous aluminosilicate that synthesised without saccharide template
MCM-41	-	Mobil Crystalline Matter 41
PAN	-	Pesticide Action Network
PUF	-	Polyurethane Foam
R^2	-	Regression coefficient
SAXS	-	Small Angle X-ray Scattering
SDS	-	Sodium Dodecylsulfate
TEOS	-	Tetraethyl Orthosilicate
TPAOH	-	Tetrapropylammonium Hydroxide
USEPA	-	United States Environmental Protection Agency

UV	-	Ultraviolet
UV-vis	-	Ultraviolet-visible Spectrophotometer
XRD	-	X-ray diffraction
XRF	-	X-ray Fluorescence
WHO	-	World Health Organization
ZSM-5	-	Zeolite Socony Mobile-5

LIST OF SYMBOLS

Å	-	Armstrong
°C	-	Degree Celsius
%	-	Percent
μm	-	Micrometer
cm^{-1}	-	Per Centimeter
cm^3/g	-	Cubic Centimeter per Gram
g	-	Gram
g/cm^3	-	Gram per Cubic Centimeter
g/mol	-	Gram per Mol
K	-	Kelvin
L	-	Liter
M	-	Molar
m^2/g	-	Square Meter per Gram
mg	-	Milligram
mg/g	-	Milligram per Gram
mg/kg	-	Milligram per Kilogram
mg/L	-	Milligram per Liter
mg/mL	-	Milligram per Milliliter
mL	-	Milliliter
mm	-	Millimeter
ng/L	-	Nanogram per Liter
nm	-	Nanometer
rpm	-	Rate per Minute

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Paraquat is a controversial pesticide under herbicide class that commonly used to control weeds. Even though the pesticide is very effective in controlling weeds however it gives adverse effect to human and environment. Paraquat is very toxic to human with lethal ingestion dosage 35 mg/kg (Extension Toxicology Network, 1993). Due to its toxicity, many poisoning cases due to paraquat were reported especially among agricultural workers (Fernandez *et al*., 2002). Not only that, some people has misused its usage as a suicide agent because ingestion of less than one tea spoon can cause fatal (Madeley, 2002). Other than that, paraquat is reported as very persistent in soil environment with field half-life more than 1000 days and it also very toxic to some aquatic life (Madeley, 2002). Since paraquat is very dangerous to human and environment, its removal from the environment has becomes an interest for many researchers (Ait Sidhoum *et al.*, 2013; Majid *et al.*, 2016; Nanseu-Njiki *et al.*, 2010; Oliveira *et al.*, 2014; Tsai and Lai, 2006). One of method for removal of paraquat is by using suitable adsorbent such as silica (Brigante and Schulz, 2011), clay (Rytwo *et al.*, 2002; Ait Sidhoum *et al.*, 2013; Seki and Yurdakoç, 2005), polymer (Vinhal *et al.*, 2015) and resin (Leite *et al*., 2013) so that the study on the ability of the adsorbent to adsorb paraquat and retained it from leached out has been performed. Besides that, study on adsorption and desorption of paraquat on adsorbent also can be applied for preconcentration method of forensic sample for suicide and poisoning cases that has trace amount of paraquat and small sample size.

Adsorbent like porous materials such as carbon, zeolites and mesoporous material has shown encouraging results for removal of paraquat. Porous materials can be divided into three categories namely microporous, mesoporous and macroporous. International Union of Pure and Applied Chemistry (IUPAC) has notated that microporous materials are materials that have pore diameters less than 2 nm while macroporous materials are for materials that have pore diameters more than 50 nm. Materials that fall under mesoporous category are those that have pore diameter that lies between 2 to 50 nm. Mesoporous material being a favour of researchers to synthesise because it has larger pore size without compromising the active sites that will promote more effective reactions. For adsorption purpose, mesoporous adsorbent will able to adsorb higher amount of analyte and larger size of compound.

Aluminosilicate is a type of material that build from element of aluminium, silicon and oxygen. The material has negative charge on the surface that come from isomorphous substitution of Al^{3+} ion for Si^{4+} ion in the silicate structure and due to dissociation of silanol groups in structural and adsorbed silicate (Perrott, 1977). This material can occur naturally or be synthesised. Zeolite is a hydrated microporous aluminosilicate material that has 3-dimensional framework with enclosing cavities and uniform channels, that occupied with water molecules and cations balancing the negatively charge of the aluminosilicate framework (Smith, 1963). This material is highly demand in industry because of its application as catalyst, adsorbent and molecular sieve (Ni *et al*., 2011; Rutkowska *et al*., 2015; Rasamimanana *et al*., 2016; Jovanovic *et al*., 2016; Razavian and Fatemi, 2015). Due to its microporous nature of zeolites, has limits its applications to smaller molecules. To enhance zeolites property for bigger molecules, many studies on converting the microporous material aluminosilicate material like zeolite to mesoporous material by using mesoporous directing agent have been done (Kadja *et al.*, 2016; Liu *et al.*, 2012; Sun *et al.*, 2015).

In this research, aluminosilicate materials having mesoporous properties was synthesised using saccharide template as mesoporous directing agent and used for adsorption and desorption of paraquat. Mesoporous aluminosilicate was chosen because it has negative charge while paraquat is positively charge, so it will be easy for mesoporous aluminosilicate to bind with paraquat. Mesoporous silica MCM-41 was chosen as comparison to the result of adsorption and desorption of paraquat using mesoporous aluminosilicate material.

1.2 Statement of Problem

Paraquat is known to be dangerous to human and our environment. Suitable material can be used as adsorbent for preconcentration of trace amount and small sample size of paraquat and for removal of it in environment. Previous researches on adsorption of paraquat have used various type of adsorbent like clays, silica, polymer, resin, and soil. Clay is material that occur naturally and composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden with dried or fired (Guggenheim and Martin, 1995). Some clay minerals consist of aluminium and silicon element and known as aluminosilicate material such as illite and bentonite mineral. Aluminosilicate material has negative charge on surface because of isomorphous substitution of Al^{3+} on Si^{4+} on the silicate structure arrangement. Paraquat is positively charge so theoretically, it can be easily bind with negatively charge aluminosilicate material and lead to effective adsorption process. Previous researches that had been done on adsorption of paraquat on aluminosilicate material only use naturally occurring aluminosilicate which is clay type materials such as bentonite, and illite, and modification of these type of materials (Seki and Yurdakoç, 2005; Ait Sidhoum *et al.*, 2013). The reported adsorption capacity range of these adsorbents is from 20 to 100 mg/g. However, this naturally occurring aluminosilicates and its modification form have a drawback since most of them were not fully characterised in order to understand the relation of the adsorption capacity with the physicochemical properties of the adsorbents. As such study need to be done using synthesised aluminosilicate material to study the relationship of the physicochemical property with adsorption capacity of paraquat.

Aluminosilicate such as zeolite is a hydrated microporous aluminosilicate material that can exist naturally or can be synthesised in the laboratory. As adsorbent for bigger molecule such as paraquat, the porous system of zeolite need to be modified from micropores to mesopores and it can be done using mesoporous directing agent such as ammonium type surfactant (Chen *et al*., 2010; Choopun and Jitkarnka, 2016; Ahmadpour and Taghizadeh, 2015; Teh *et al*., 2015), carbon material (Koo *et al.*, 2010; Pavlačková *et al.*, 2006) and saccharide (Jin *et al.*, 2016; Ma *et al*., 2013; Wang *et al.*, 2009; Zhang *et al.*, 2016) to improve its properties by having larger pore size so it can absorb higher amount of paraquat. Compare to another mesoporous directing agents, saccharide is less expensive and environmental friendly. By using synthesised aluminosilicate material such as zeolite with mesoporous characteristic, the adsorption capacity of paraquat on the adsorbents can be studied and compare to previous researches that had been done that use naturally occurring aluminosilicate material and its modified form.

1.3 Objective of Study

The objectives of this study are:

1. To synthesise different type of mesoporous aluminosilicate materials using various saccharide template.
2. To characterise the as-synthesised mesoporous materials to confirm the formation of synthesised materials.
3. To study the adsorption and desorption ability of paraquat on synthesised mesoporous materials.

1.4 Scope of Study

In this study, the mesoporous aluminosilicates were synthesised using saccharides templates as mesoporous directing agent namely glucose, sucrose and lactose. The mesoporous aluminosilicate without saccharide template also had been synthesised to compare the result between with and without presence of saccharide template. The source of silica that was used is from tetraethyl orthosilicate (TEOS) and the alumina source comes from aluminium sulphate octadecahydrate, $Al_2(SO_4)_3.18H_2O$. For MCM-41, the silica source that was used is Ludox solution and cetyltrimethylammonium bromide (CTABr) act as cationic surfactant.

The adsorption and desorption experiment was done in batch sorption method. The parameter that have been studied for adsorption part were adsorption time and initial concentration of paraquat. The isotherm of adsorption study was done based on the result of the initial concentration of paraquat parameter and analysed using Langmuir and Freundlich isotherm. Effect of different desorption method was studied for desorption part.

1.5 Significance of Study

The purpose of this study is to study the adsorption and desorption of paraquat on mesoporous materials. One of the significance of this research is the mesoporous material that has larger size of pores so it can absorb larger size of compound and higher amount of analyte. Other than that, aluminosilicate is negatively charged so it is good to be used as an adsorbent for adsorption of paraquat because paraquat is positively charged, so it will easily bind to aluminosilicate material. In this research, saccharide templates were used in synthesising mesoporous aluminosilicate as mesoporous directing agent and the advantages of using saccharides as template are there are cheap and environmental friendly template.

The other significance of this research is by studying the adsorption and desorption ability of synthesised mesoporous materials on paraquat, the materials can be applied as adsorbent for removal of paraquat in environment and for preconcentration of trace amount of paraquat in small sample size *i.e.* in forensic sample prior to analysis using less expensive instrument like ultraviolet-visible spectrophotometer that will reduce the cost of analysis.

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