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Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater

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Additional information is available at the end of the chapter

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1. Introduction

Organic pollution is the term used when large quantities of organic compounds. It originates from domestic sewage, urban run-off, industrial effluents and agriculture wastewater. sewage treatment plants and industry including food processing, pulp and paper making, agriculture and aquaculture. During the decomposition process of organic pollutants the dissolved oxygen in the receiving water may be consumed at a greater rate than it can be replenished, causing oxygen depletion and having severe consequences for the stream biota. Wastewater with organic pollutants contains large quantities of suspended solids which reduce the light available to photosynthetic organisms and, on settling out, alter the characteristics of the river bed, rendering it an unsuitable habitat for many invertebrates. Organic pollutants include pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals, proteins and carbohydrates [1-3].

Toxic organic pollutants cause several environmental problems to our environment. The most common organic pollutants named persistent organic pollutants (POPs). POPs are compounds of great concern due to their toxicity, persistence, long-range transport ability [4] and bioaccumulation in animals [5], travel long distances and persist in living organisms. POPs are carbon-based chemical compounds and mixtures (twelve pollutants) that include industrial chemicals such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), and some organochlorine pesticides (OCPs), such as hexachlorobenzene (HCB) or dichloro-diphenyl-trichloroethane (DDT), dibenzo-p-dioxins (dioxins) and dibenzo-p-furans (furans) [6]. PCDD/Fs are released to the environment as by-products of several processes, like waste incineration or metal production [7]. Many of these compounds have been or continue to be used in large quantities and due to their environmental persistence, have the ability to bioaccumulate and biomagnify [8].

Efficient techniques for the removal of highly toxic organic compounds from water have drawn significant interest. A number of methods such as coagulation, filtration with coagulation, precipitation, ozonation, adsorption, ion exchange, reverse osmosis and advanced oxidation processes have been used for the removal of organic pollutants from polluted water and wastewater. These methods have been found to be limited, since they often involve high capital and operational costs. On the other hand ion exchange and reverse osmosis are more attractive processes because the pollutant values can be recovered along with their removal from the effluents. Reverse osmosis, ion exchange and advanced oxidation processes do not seem to be economically feasible because of their relatively high investment and operational cost.

Among the possible techniques for water treatments, the adsorption process by solid adsorbents shows potential as one of the most efficient methods for the treatment and removal of organic contaminants in wastewater treatment. Adsorption has advantages over the other methods because of simple design and can involve low investment in term of both initial cost and land required. The adsorption process is widely used for treatment of industrial wastewater from organic and inorganic pollutants and meet the great attention from the researchers. In recent years, the search for low-cost adsorbents that have pollutant-binding capacities has intensified. Materials locally available such as natural materials, agricultural wastes and industrial wastes can be utilized as low-cost adsorbents. Activated carbon produced from these materials can be used as adsorbent for water and wastewater treatment [9].

2. Adsorption phenomenon

Adsorption is a surface phenomenon with common mechanism for organic and inorganic pollutants removal. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid-solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited at the solid surface. The solute retained (on the solid surface) in adsorption processes is called adsorbate, whereas, the solid on which it is retained is called as an adsorbent. This surface accumulation of adsorbate on adsorbent is called adsorption. This creation of an adsorbed phase having a composition different from that of the bulk fluid phase forms the basis of separation by adsorption technology.

In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak Van Der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction.

As the adsorption progress, an equilibrium of adsorption of the solute between the solution and adsorbent is attained (where the adsorption of solute is from the bulk onto the adsorb-

ent is minimum). The adsorption amount (q_e , mmol g^{-1}) of the molecules at the equilibrium step was determined according to the following equation:

$$q_e = V(C_0 - C_e) / M \quad (1)$$

where V is the solution volume (L); M is the mass of monolithic adsorbents (g); and C_0 and C_e are the initial and equilibrium adsorbate concentrations, respectively.

Other definition of adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions. Large surface area leads to high adsorption capacity and surface reactivity [10].

2.1. Adsorption isotherms and models

An adsorption isotherm is the presentation of the amount of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the bulk solution at constant temperature. Langmuir and Freundlich adsorption isotherms are commonly used for the description of adsorption data.

The Langmuir equation is expressed as:

$$C_e / q_e = 1 / bX_m + C_e / X_m, \quad (2)$$

Where C_e is the equilibrium concentration of solute (mmol L^{-1}), q_e is the amount of solute adsorbed per unit weight of adsorbent (mmol g^{-1} of clay), X_m is the adsorption capacity (mmol g^{-1}), or monolayer capacity, and b is a constant (L mmol^{-1}).

The Freundlich isotherm describes heterogeneous surface adsorption. The energy distribution for adsorptive sites (in Freundlich isotherm) follows an exponential type function which is close to the real situation. The rate of adsorption/desorption varies with the strength of the energy at the adsorptive sites. The Freundlich equation is expressed as:

$$\log q_e = \log k + 1/n \log C_e, \quad (3)$$

Where k (mmol g^{-1}) and $1/n$ are the constant characteristics of the system [11].

3. Types of adsorbents

Different types of adsorbents are classified into natural adsorbents and synthetic adsorbents. Natural adsorbents include charcoal, clays, clay minerals, zeolites, and ores. These natural materials, in many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities. Syn-

thetic adsorbents are adsorbents prepared from Agricultural products and wastes, house hold wastes, Industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Many waste materials used include fruit wastes, coconut shell, scrap tyres, bark and other tannin-rich materials, sawdust, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil, ore minerals etc.

Activated carbons as adsorbent for organic pollutants consists in their adsorption a complex process and there still exists considerable difficulty. The main cause of this difficulty results from the large number of variables involved. These include, for example, electrostatic, dispersive and chemical interactions, intrinsic properties of the solute (for example solubility and ionization constant), intrinsic properties of the adsorbent (such pore size distribution), solution properties (in particular, pH) and the temperature of the system [12].

Activated carbons (AC) (both granular activated carbon (GAC) and powdered activated carbons (PAC)) are common adsorbents used for the removal of undesirable odor, color, taste, and other organic and inorganic impurities from domestic and industrial waste water owing to their large surface area, micro porous structure nonpolar character and due to its economic viability. The major constituent of activated carbon is the carbon that accounts up to 95% of the mass weight. In addition, active carbons contain other hetero atoms such as hydrogen, nitrogen, sulfur, and oxygen. These are derived from the source raw material or become associated with the carbon during activation and other preparation procedures [13-14]. Putra et al. [15] investigated the removal of Amoxicillin (antibiotic) from pharmaceutical effluents using bentonite and activated carbon as adsorbents. The study was carried out at several pH values. Langmuir and Freundlich models were then employed to correlate the equilibria data on which both models fitted the data equally well. While chemisorption is the dominant adsorption mechanism on the bentonite, both physisorption and chemisorption played an important role for adsorption onto activated carbon.

Adsorption of methane on granular activated carbon (GAC) was studied. The results showed that with decreasing temperature or increasing methane uptake by GAC the adsorption efficacy decreased. Interactions between the methane molecules and the surface of carbon increase the density of adsorbed methane in respect to the density of compressed gas. The effect that the porosity and the surface chemistry of the activated carbons have on the adsorption of two VOC (benzene and toluene) at low concentration (200 ppm) was also studied. The results show that the volume of narrow micropores (size <0.7 nm) seems to govern the adsorption of VOC at low concentration, specially for benzene adsorption. AC with low content in oxygen surface groups has the best adsorption capacities. Among the AC tested, those prepared by chemical activation with hydroxides exhibit the higher adsorption capacities for VOC. The adsorption capacities achieved are higher than those previously shown in the literature for these conditions, especially for toluene. Adsorption capacities as high as 34 g benzene/100 g AC or 64 g toluene/100 g AC have been achieved [16].

4. Adsorption of dyes

Adsorption techniques are used as high quality treatment processes for the removal of dissolved organic pollutants, such as dyes, from industrial wastewater. Dyes consider as type of organic pollutants. The textile, pulp and paper industries are reported to utilize large quantities of a number of dyes, these pollutant may be found in wastewaters of many industries generating considerable amounts of colored wastewaters, toxic and even carcinogenic, posing serious hazard to aquatic living organisms. Dyes represent one of the problematic groups; they are emitted into wastewater from various industrial branches, mainly from the dye manufacturing and textile finishing and also from food coloring, cosmetics, paper and carpet industries. It is well known that the dye effluents from dyestuff manufacturing and textile industries, may exhibit toxic effects on microbial populations and can be toxic and/or carcinogenic to mammalian animal. Most dyes used in textile industries are stable to light and are not biologically degradable. Furthermore, they are resistant to aerobic digestion. [17].

On searching for economical and available starting materials; different low cost adsorbents were used for the removal of dyes. Activated rice husk was used as cheap adsorbent for color removal from wastewater [18]. Hamdaoui [19] reported that the maximum adsorption of basic dye, methylene blue, onto cedar sawdust and crushed brick was 60 and 40 mg L⁻¹, respectively. Wood-shaving bottom ash (WBA) was used for the removal of Red Reactive 141 (RR141), and azo reactive dyes. WBA/H₂O and WBA/H₂SO₄ adsorbents were made by treating WBA with water and 0.1 M H₂SO₄, respectively; to increase adsorption capacity. The effects of different parameters on adsorption (effect of contact time, initial pH of solution, dissolved metals and elution) were studied. The maximum dye adsorption capacities of WBA/H₂O and WBA/H₂SO₄ obtained from a Langmuir model at 30 °C were 24.3, 29.9, and 41.5 mg l⁻¹, respectively. In addition, WBA/H₂O and WBA/H₂SO₄ could reduce colour and high chemical oxygen demand (COD) of real textile wastewater [20]. Beer brewery waste has been shown to be a low-cost adsorbent for the removal of methylene blue dye from the aqueous solution. The results of preliminary adsorption kinetics showed that the diatomite waste could be directly used as a potential adsorbent for removal of methylene blue on the basis of its adsorption–biosorption mechanisms [21].

Sewage sludge was applied for the preparation of activated carbon adsorbent. Activated carbon adsorbent prepared from sewage sludge has being identified as a potentially attractive material for wastewater. Research studies has been conducted to demonstrate the uses of treated sewage sludge for the removal of dyes from wastewater and polluted water [22-27]. Otero et al. [27] produced activated carbon by chemically activation and pyrolysis of sewage sludge. The properties of this type of material was studied by liquid-phase adsorption using crystal violet, indigo carmine and phenol as adsorbates. Three prepared activated carbon, of different particle sizes, were used ASS-g1 (particle diameter < 0.12 mm), ASS-g2 (0.12 < particle diameter < 0.5 mm) and PSS-g2 (0.12 < particle diameter < 0.5 mm). Crystal violet dye adsorption has been higher (Q_{max} 263.2 mg/g using AAS, 270 mg/g using ASS and 184 mg/g using PPS) than indigo carmine (Q_{max} 60.04 mg/g using AAS, 54.8 mg/g using ASS and 30.8 mg/g

using PPS). They proposed that activated carbons made from sewage sludge show promise for the removal of organic pollutants from aqueous streams.

Dye	Adsorbent	Adsorption capacity	Reference
Reactive Blue 2	activated carbon	0.27,mmol/g	[31]
Reactive Red 4,	activated carbon	0.24 mmol/g	[31]
Reactive Yellow 2	activated carbon	0.11 mmol/g	[31]
Everzol Black B	Sepiolite	120.5 g/kg	[32]
Everzol Red 3BS	Sepiolite	108.8 g/kg	[33]
Everzol Red 3BS	Zeolite	111.1 g/kg	[32]
Everzol Black B	Zeolite	60.6 g/kg	[32]
Orange-G	bagasse fly ash	1.245 g/kg	[33]
Methyl Violet	bagasse fly ash	3.712 g/kg	[33]
Acid Blue 113	amino-functionalized nanoporous silica SBA-3	769 g/kg	[34]
Acid Red 114	amino-functionalized nanoporous silica SBA-3	1000 g/kg	[34]
Acid Green 28	amino-functionalized nanoporous silica SBA-3	333 g/kg	[34]
Acid Yellow 127	amino-functionalized nanoporous silica SBA-3	1250 g/kg	[34]
Acid Orange 67	amino-functionalized nanoporous silica SBA-3	2500 g/kg	[34]
Acid Blue 25	waste tea activated carbon	203.34 mg/g	[35]
Methylene Blue	bituminous coal-based activated carbon	580 mg/g	[36]
Methylene Blue	coal-based activated carbon coal-based activated carbon(KOH washed)	(252 mg/g 234.0 mg/g)	[37]
Methylene Blue	activated carbon from Cotton stalk-based	180.0 mg/g	[38]
Methylene Blue	activated carbon from Posidonia oceanica (L.) dead leaves:	285.7 mg/g	[39]
Methylene Blue	Salix psammophila activated carbon	225.89 mg/g	[40]

Dye	Adsorbent	Adsorption capacity	Reference
Methylene Blue	activated carbon from flamboyant pods (<i>Delonix regia</i>)	890mg/g	[41]
Methylene Blue	activated carbon from from Oil palm wood-based	90.9 mg/g	[42]
Methylene Blue	activated carbon from Oil palm shell-based	243.9 mg/g	[43]

Table 1. Selected adsorbents used for dyes removal from polluted water

The utilization of fly ash in removing dyes from textile wastewater was investigated. A calcium-rich fly ash had been used as adsorbent for the removal of Congo red dye under different conditions. It was observed that the maximum adsorption obtained was between 93% and 98%. under the studies conditions [28]. Wang et al. [29] had reported the use of treated and non-treated fly ash for the removal of methylene blue and basic dye from a wastewater solution. The adsorption capacity for acid treated fly ash was found to be 2.4×10^{-5} mol/g, while non-treated fly ash showed an adsorption capacity of 1.4×10^{-5} mol/g. Wang et al. [30] in another investigation also found that the porous unburned carbon in the fly ash was responsible for the adsorption of the dye, and not the fly ash itself. Table (1) shows selected adsorbent used for dyes removal from polluted water

5. Adsorption of phenols

Since 1860, phenol has been in production, with its basic use as an antiseptic. During late 19th century and thereafter the use of phenol has been further extended to the synthesis of dyes, aspirin, plastics, pharmaceuticals, petrochemical and pesticide chemical industries. In fact, by 2001, the global phenol production has reached an impressive 7.8 million tons [44].

Among the different organic pollutants in wastewater, phenols are considered as priority pollutants since they are harmful to plants, animals and human, even at low concentrations. The major sources of phenolic are steel mills, petroleum refineries, pharmaceuticals, petrochemical, coke oven plants, paints, coal gas, synthetic resins, plywood industries and mine discharge. The wastewater with the highest concentration of phenol (>1000 mg/L) is typically generated from coke processing. Phenolic compounds are also emanated from resin plants with a concentration range of 12–300 mg/L. Environmental Protection Agency (EPA) has set a limit of 0.1 mg/L of phenol in wastewater. The World Health Organization (WHO) is stricter on phenol regulation. It sets a 0.001 mg/L as the limit of phenol concentration in potable water.

Adsorption of phenolic compounds from aqueous solutions by activated carbon is one of the most investigated of all liquid-phase applications of carbon adsorbents [45]. Several ad-

sorbents were used treatment wastewater and removal of phenols. The adsorption isotherms for mono-, di-, and trichlorophenols from aqueous solutions on wood-based and lignite-based carbons were investigated. The adsorptive capacity for 2,4-DCP was found to be 502 mg/g and Freundlich model gave a best fit the experimental data [46]. Zogorski et al. [47] studied the kinetics of adsorption of phenols on GAC. They observed that 60% to 80% of the adsorption occurs within the first hour of contact followed by a very slow approach to the final maximum equilibrium concentration.

In another study, the extent of adsorption of 2,4-dichlorophenol was found to be a function of pH. The presence of surface functional groups also affected the adsorption of phenols onto activated carbon. The presence of dissolved oxygen on activated carbon increased the adsorptive capacity for phenolic compounds. This increase in adsorptive capacity was attributed to the oligomerization of the compounds through oxidative coupling reactions [48].

Hamdaouia et al. [49] studied and modeled the adsorption equilibrium isotherms of five phenolic compounds from aqueous solutions onto GAC. The five compounds selected were Phenol (Ph), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). They also observed that the interaction of phenolic compounds with activated carbon surface occurred in localized monolayer adsorption type, i.e. adsorbed molecules are adsorbed at definite, localized sites. Uptake of phenols increased in the order $\text{Ph} < 2\text{-CP} < 4\text{-CP} < \text{DCP} < \text{TCP}$, which correlated well with respective increase in molecular weight, cross-sectional area, and hydrophobicity and decrease in solubility and pKa.

Sawdust, a very low cost adsorbent was used, after carbonization, for the removal of phenol from industrial waste waters. The equilibrium adsorption level was determined as a function of the solution pH, temperature, contact time, adsorbent dose and the initial concentration. The adsorption maximum for phenol using sawdust was 10.29 mg/L [50].

Adsorbents, carbonaceous materials, activated carbon (AC), bagasse ash (BA) and wood charcoal (WC), were used for removal of phenol from water [51]. The results showed the removal efficiencies for phenol-AC, phenol-WC and phenol-BA, approximately 98%, 90% and 90%, respectively. Removal efficiency of phenol slightly increased when the pH of adsorption system decreased. Yapar and Yilmaz [52] reported the adsorptive capacity of some clays and natural zeolite materials found in Turkey for the removal of phenol. They found that calcined hydrotalcite was the best among the studied adsorbents in which adsorbed 52% of phenol from a solution of 1000 mg/L phenol at the adsorbent/phenol ratio of 1:100 while the others adsorbed only 8% of phenol. Also, silica gel, activated alumina, AC, fitrasorb 400 and Hisir 1000 adsorbent were examined as adsorbents for the removal of phenol from aqueous solution. They found that Hisir 1000 was the best among the tested materials [53]. Das and Patnaik [54] utilized blast furnace flue dust (BFD) and slag to investigate phenol adsorption through batch experiment.

Bromophenols (2-bromophenol, 4-bromophenol and 2, 4- dibromophenol) considered as one of toxic organic phenol. Industrial wastes was used as low cost adsorbent for the removal of these pollutants. The results show the maximum adsorption on carbonaceous adsorbent prepared from fertilizer industry waste 40.7, 170.4 and 190.2 mg g⁻¹ for 4-bromophenol 2-bro-

mophenol and 2, 4-dibromophenol, respectively. As compared to carbonaceous adsorbent, the other three adsorbents (viz., blast furnace sludge, dust, and slag) adsorb bromophenols to a much smaller extent [55]. Table (2) represented the adsorption efficiencies of different adsorbents for the removal of phenols.

Organic Pollutants	Adsorbent	Adsorption Maxmium	Ref.
Phenol	Porous Clay	14.5 mg/g	[56]
2,5-dichlorophenol	Porous Clay	45.5 mg/g	[56]
3,4-dichlorophenol	Porous Clay	48.7 mg/g	[56]
3,5-dichlorophenol	(cetyl-pyridinium-Al PILC),	97.2 mg/g	[57]
phenol	Hemidesmus Indicus Carbon(HIC)	370 ppm	[58]
phenol	Commercial Activated Carbon(CAC)	294 ppm	[58]
phenol	NORIT Granular Activated Carbon (NAC 1240)	74.07 mg/g	[59]
phenol	NORIT Granular Activated Carbon 1010	166.6 mg/g	[59]
phenol	Active carbon	257 mg/g	[60]
phenol	Mesoporous carbon CMK-3-100°C	347 mg/g	[60]
phenol	Mesoporous carbon CMK-3-130 °C	428 mg/g	[60]
phenol	Mesoporous carbon CMK-3-150 °C	473 mg/g	[61]
phenol	Leaf litter of <i>Shorea roubsta</i>	76%	[60]
phenol	activated phosphate rock (1M HNO3)	83.34 mg/g	[62]
phenol	Natural clay	15 mg/g	[63]
2,4-dichlorophenol	activated carbon derived from oil palm empty fruit bunch (EFB)	232.56 mg/g	[64]

Table 2. Adsorption capacities of different adsorbents for the removal of phenols.

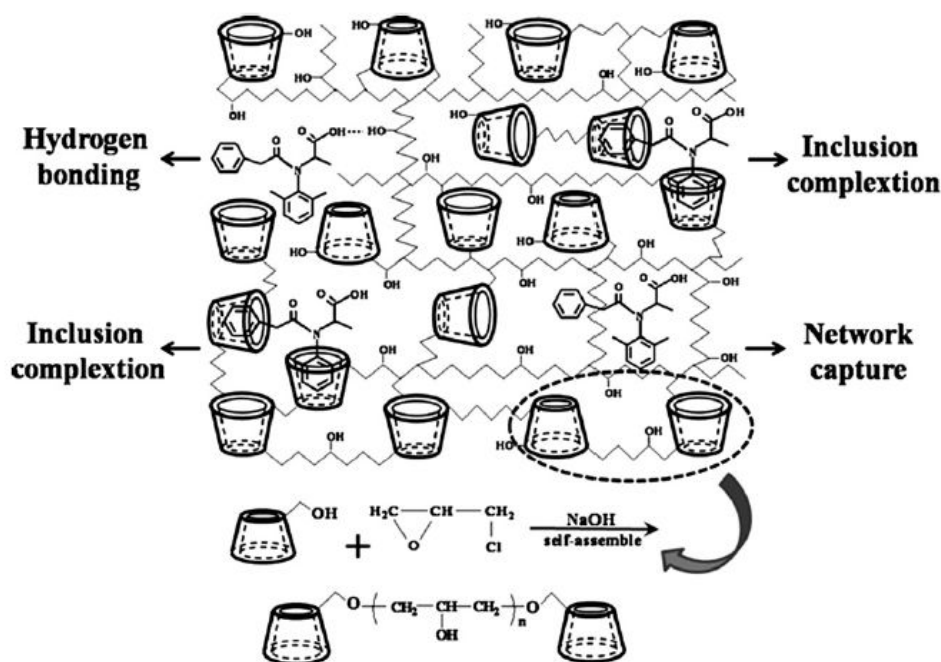
6. Adsorption of pesticides and herbicides

Pesticides and herbicides, intentionally released into the environment, are ubiquitous in aquatic systems; they are often detected at low levels and commonly occur in the form of complex mixtures [64-65]. Leaching of chemical fertilizers and pesticides, applied to agricultural and forest land, is one of the main reasons for organic pollution in several water streams. Pesticides and herbicides are harmful to life because of their toxicity, carcinogenicity and mutagenicity [66]. Therefore toxicity of pesticides and their degradation products is making these chemical substances a potential hazard by contaminating the environment. They have raised serious concerns about aquatic ecosystem and human health because of

the long-term accumulation of their single and/or combined toxicological effects [67]. The contamination of ground water, surface water and soils, by pesticides and herbicides are currently a significant concern, and this because of increasing use of pesticides in agriculture, and domestic activities [68].

Among newly developed pesticides, organophosphorous pesticides are most commonly used. This class of chemicals is divided into several forms; however the two most common forms are phosphates and phosphorothionates. Methyl parathion (O,O-dimethyl O-4-nitrophenyl phosphorothioate) is a class I insecticide. Once methyl parathion introduced into the environment from spraying on crops, droplets of methyl parathion in the air fall on soil, plants or water. While most of the methyl parathion will stay in the areas where it is applied, some can move to areas away from where it was applied by rain, fog and wind [69].

Modified polymer adsorbents were prepared for the removal of organic pollutants from water and wastewater. Adsorption of organic pollutants using cyclodextrin-based polymer (CDPs) as adsorbent, is an efficient technique with the advantages of specific affinity, low cost and simple design [65, 70-71]. Cyclodextrin polymers (CDPs) can be synthesized using cyclodextrin (CD) as complex molecule and polyfunctional substance (e.g., epichlorohydrin (EPI)) as cross-linking agent. Though a number of CDPs with various structures and properties have been developed [72,73], it is still ambiguous how CDP properties affect adsorption affinity toward organic contaminants, particularly mixed pollutants. Liu et al. [66] illustrated the cross-linked structure of cyclodextrin polymer and related adsorption mechanisms in Scheme (1).



Scheme 1. Cross-linked structure of cyclodextrin polymer and related adsorption mechanisms, from Liu et al. [66].

Other modified polymer adsorbent was used in herbicides treatment, porous polymeric adsorbents were used for the adsorption of herbicides (alachlor, amitrole, trifluralin and prometryn) from liquid solution. Two adsorbent resins were investigated, the highly hydrophobic Amberlite XAD-4 (polystyrene–divinylbenzene copolymer) and the functionalized more hydrophilic XAD-7 (nonionic aliphatic acrylic polymer). The adsorption were successfully at pH 6.5 [74].

Other adsorbent used widely for the removal of pesticides is activated carbon. Activated carbons (ACs) prepared from agricultural and industrial wastes were used for the removal of pesticides from polluted water. Activated carbons produced from agricultural residues (olive kernel, corn cobs, rapeseed stalks and soya stalks) via physical steam activation were tested for the removal of Bromopropylate (BP) pesticide from water. The results show maximum adsorption capacity (q_m) of the pesticide on adsorbents (ACs) prepared from corn cob, olive kernel, soya stalks and rapeseed stalks at values 7.9×10^{-2} , 12.3×10^{-2} , 11.6×10^{-2} and 18.9×10^{-2} mmol/L, respectively. The BP removal from water achieved in this study was 90–100% for all ACs [75].

Ayranci and Hoda [76] studied the adsorption of pesticides, pesticides ametryn [2-(ethylamino)-4-isopropylamino-6-methyl-thio-s-triazine], aldicarb (2-methyl-2-(methylthio) propionaldehyde o-methylcarbamoyloxime], diuron [N-(3,4-dichlorophenyl)- N,N-dimethyl urea] and dinoseb [2-(sec-butyl)- 4,6-dinitrophenol], from aqueous solution onto high specific area activated carbon-cloth adsorbent (ACC) and found that the maximum adsorption capacity of ACC for ametryn, diuron, dinoseb and aldicarb were 354.61, 421.58, 301.84 and 213.06 mg/g, respectively.

Djilani et al. [77] developed new activated carbon adsorbents from lignocellulosic wastes of vegetable origin (coffee grounds (CG), melon seeds (MS) and orange peels (OP)). The adsorption efficiency of these new adsorbents was tested with organic pollutants: o-nitrophenol and p-nitrotoluene. The elimination ratio obtained with new adsorbents was in the range from 70% to 90%. The time necessary to attain the adsorption equilibrium was between 75 and 135 min.

The ability of MgAl layered double hydroxides (LDHs) and their calcined products to adsorb pesticides contaminants, 2,4-dinitrophenol (DNP) and 2-methyl-4,6-dinitrophenol (DNOC) from water was assessed. Adsorption tests were conducted on LDHs with variable Mg/Al ratios (and variable layer charge), pH values, contact times and initial pesticide concentrations to identify the optimum conditions for the intended purpose. All adsorbents except the carbonate-containing hydrotalcite possessed a very high adsorption capacity for both contaminants. As noted above, the adsorption of the pesticides on the calcined LDHs was only 25–40% [78]

Activated carbon prepared from banana stalk by potassium hydroxide (KOH) and carbon dioxide (CO₂) activation (BSAC) was explored for its ability to remove the pesticides, 2,4-dichlorophenoxyacetic acid (2,4-D) and bentazon. The percent removal efficiency of 2,4-D decreased from 98.4 to 85.4% as the 2,4-D initial concentration increased from 50 to 300 mg L⁻¹. For bentazon, the percent removal efficiency decreased from 96.5 to 61.6% as the bentazon

initial concentration increased from 25 to 250 mg L⁻¹. Therefore, the adsorption of 2,4-D and bentazon by BSAC has strong dependence on the initial concentration of the pesticides. Maximum adsorption capacity (q_e) for 2,4-dichlorophenoxyacetic acid (2,4-D) were 168.03 mg g⁻¹, and for bentazon 100.95 mg g⁻¹ [79]

In the other study for using activated carbon as adsorbent, magnetic and graphitic carbon nanostructures was used for the removal of a pesticide (2,4-dichlorophenoxyacetic acid) from aqueous solution. The magnetic and graphitic carbon nanostructures as adsorbents were prepared from two different biomasses, cotton and filter paper. The resultant adsorbents were characterized with TEM and N₂ adsorption–desorption methods. The adsorption capacities for the prepared adsorbents from filter paper and cotton are about 77 and 33 mg/g, respectively [80].

Chemically and thermally treated watermelon peels (TWMP) have been utilized for the removal of methyl parathion (MP) pesticide from water. The effect of process variables such as pH of solution, shaking speed, shaking time, adsorbent dose, concentration of solution and temperature have been optimized. Maximum adsorption (99±1%) was achieved for (0.38–3.80)×10⁻⁴ mol dm⁻³ of MP solution, using 0.1 g of adsorbent in 20 ml of solution for 60 min agitation time at pH 6. The developed adsorption method has been employed to surface water samples with percent removal 99%±1 [81].

7. Adsorption of other organic pollutants

Other organic pollutants were found as a pollutants in water and wastewater, this include pharmaceutical effluents, surfactants, organic solvents, phthalates, hydrocarbons, esters, alcohols, volatile, semi-volatile and non-volatile chlorinated organic pollutants. Activated carbons, calys and clay minerals are used widely for the removal of organic pollutants.

7.1. Adsorption on activated carbon

Adsorption on activated carbon is currently the most frequently used technology for removing organic pollutants from aqueous industrial sludge, surface waters and drinking water. Methyl tert-butyl ether (MTBE) is an organic pollutants used mainly as a fuel component in fuel if gasoline engine and also as a solvent. The adsorption of methyl tert-butyl ether (MTBE) by granular activated carbon was investigated, the maximum adsorption capacity of MTBE on granular activated carbon was 204.1 mg/g. Results illustrate that granular activated carbon is an effective adsorbent for methyl tert-butyl ether and also provide specific guidance into adsorption of methyl tert-butyl ether on granular activated carbon in contaminated groundwater [82].

A novel triolein-embedded activated carbon composite adsorbent was developed. Results suggested that the novel composite adsorbent was composed of the supporting activated carbon and the surrounding triolein-embedded cellulose acetate membrane. The adsorbent was stable in water, for no triolein leakage was detected after soaking the adsorbent for five

weeks. The adsorbent had good adsorption capability to dieldrin, which was indicated by a residual dieldrin concentration of $0.204 \mu\text{gL}^{-1}$. The removal efficiency of the composite adsorbent was higher than the traditional activated carbon adsorbent [83]. Essa et al. [84] studied the potential of chemical activated date pits as an adsorbent. The date pits were impregnated with 70% phosphoric acid followed by thermal treatment between 300 to 700°C . The effects of activation temperature and acid concentration on pore surface area development were studied. Samples prepared at 500°C showed a specific area of $1319 \text{ m}^2/\text{g}$ and total pore volume of $0.785 \text{ cm}^3/\text{g}$. Aqueous phenol adsorption trends using the local activated carbon sample were compared to a commercial sample (Filtrisorb-400).

Five commercially available types of activated carbon (GAC 1240, GCN 1240, RB 1, pK 1-3, ROW 0.8 SUPRA)are prepared and used to remove organic chlorinated compounds from wastewater of a chemical plant. The various types of activated carbon were tested on the basis of Freundlich adsorption isotherms for 14 pure organic chlorinated compounds, of molecular weight ranging from that of dichloromethane ($\text{MW } \frac{1}{4} 84.93 \text{ g mol}^{-1}$) to hexachlorobenzene ($\text{MW } \frac{1}{4} 284.78 \text{ g mol}^{-1}$). The best adsorbent (GAC 1240 granulated activated carbon) was selected and used in a laboratory fixed bed column to assess its removal efficiency with respect to the tested organic chlorinated compounds. Removal efficiency was always higher than 90% (Table 3) [85]

Substance	Precentage of adsorption efficiency (%)
Dichloromethane	98.3
Trichloromethane	98.8
1,1,1- Trichloromethane	99.0
Carbon tetrachloride	99.0
1,2-Dichloroethane	82.8
Trichloroethylene	94.7
1,1,2- Trichloroethane	86.3
Tetrachloroethylene	91.6
1,1,1,2- Tetrachloroethane	87.3
Trans 1,4-dichloro-2-butene	94.2
1,2,4-Trichlorobenzene	99.2
1,2,3-Trichlorobenzene	90.5
Hexachloro-1,3-butadiene	99.4
Hexachlorobenzene	95.1

Table 3. Removal efficiency (%) of chlorinated compounds from wastewater by five commercially available types of activated carbon, from Pavonia et al [85]

Antibiotic considered as one of the pharmacological organic pollutants. Choi et al. [86] investigated the treatment of seven tetracycline classes of antibiotic (TAs) from raw waters (synthetic and river) using coagulation and granular activated carbon (GAC) filtration. Their results ended to that both coagulation and GAC filtration were effective for the removal of TAs, and the

removal efficiency depended on the type of TAs. GAC filtration was relatively more effective for removal of tetracycline (TC), doxycycline-hyclate (DXC), and chlortetracycline-HCl (CTC), which were difficult to be removed by coagulation. Putra et al. [87] investigated the removal of Amoxicillin (antibiotic) from pharmaceutical effluents using bentonite and activated carbon as adsorbents. The study was carried out at several pH values. Langmuir and Freundlich models were then employed to correlate the equilibria data on which both models fitted the data equally well. While chemisorption is the dominant adsorption mechanism on the bentonite, both physisorption and chemisorption played an important role for adsorption onto activated carbon. Ruiz et al. [88] studied the removal of paracetamol (anti analgesic drug) from aqueous solutions using chemically modified activated carbons. The effect of the chemical nature of the activated carbon material such as carbon surface chemistry and composition on the removal of paracetamol was studied. The surface heterogeneity of the carbon affected the rate of paracetamol removal. They found that after oxidation the wettability of the carbon was enhanced, which favored the transfer of paracetamol molecules to the carbon pores. At the same time the overall adsorption rate and removal efficiency are reduced in the oxidized carbon due to the competitive effect of water molecules. Tris (2-chloroethyl) phosphate (TCEP), iopromide, naproxen, carbamazepine, and caffeine drugs were quite frequently observed in both surface waters and effluents from waste water treatment plants. The elimination of these chemicals during drinking water and wastewater treatment processes at full- and pilot-scale also was investigated. Conventional drinking water treatment methods such as flocculation and filtration were relatively inefficient for contaminant removal, while efficient removal (99%) was achieved by granular activated carbon (GAC).

Liu et al. [89] studied the removal effects of organic pollutants in drinking water (42 species organic pollutants in 11 categories) by activated carbon, haydite and quartz sand with the method of solid-phase extraction (SPE). The removal rates of total peak area of organic pollutants by activated carbon, haydite and quartz were 70.35%, 29.68% and 37.36%. Among all, activated carbon showed the best removal effect to most organic pollutants contents, and quartz sand to species. So if activated carbon - quartz sand combined processes were adopted, organic pollutants species and total peak area could be reduced simultaneously. The removal rates for phthalates, hydrocarbons, esters and alcohols were 62.62%, 75.83%, 72.52% and 62.99%, respectively. The adsorption capability of activated carbon for dimethyl phthalate and di-n-butyl phthalate, two priority pollutants in water, were preferable. The removal rates reached 93.27% and 57.02%. For haydite, there were 26 kinds of organic pollutants in 10 categories in corresponding treated water. The total peak area was removed by 29.68%. The removal effects for amines, alkanes and phenols were satisfactory and the removal rates were 68.71%, 49.97% and 41.19%, respectively. But in the case of phthalates, esters and aldehydes the effects were not obviously, the same as dimethyl phthalate and di-n-butyl phthalate. The species of organic pollutants were reduced from 36 to 20 by quartz sand. Most notably, xylene, dimethyl phthalate and di-n-butyl phthalate in raw water were removed efficiently. Xylene and di-n-butyl phthalate in tap water were removed absolutely, and dimethyl phthalate was removed by 59.59%.

Cellulose acetate (CA) embedded with triolein (CA-triolein), was prepared as adsorbent for the removal of persistent organic pollutants (POPs) from micro-polluted aqueous solution. The comparison of CA-triolein, CA and granular activated carbon (GAC) for dieldrin removal was investigated. Results showed that CA-triolein adsorbent gave a lowest residual concentration after 24 h although GAC had high removal rate in the first 4 h adsorption. Then the removal efficiency of mixed POPs (e.g. aldrin, dieldrin, endrin and heptachlor epoxide), absorption isotherm, adsorbent regeneration and initial column experiments of CA-triolein were studied in detail. The linear absorption isotherm and the independent absorption in binary isotherm indicated that the selected POPs are mainly absorbed onto CA-triolein adsorbent by a partition mechanism. Thermodynamic calculations showed that the absorption was spontaneous, with a high affinity and the absorption was an endothermic reaction. Rinsing with hexane the CA-triolein adsorbent can be regenerated after absorption of POPs. No significant decrease in the dieldrin removal efficiency was observed even when the absorption-regeneration process was repeated for five times. The results of initial column experiments showed that the CA-triolein adsorbent did not reach the breakthrough point at a breakthrough empty-bed volume (BV) of 3200 when the influent concentration was 1–1.5 g/L and the empty-bed contact time (EBCT) was 20 min [90]

Activated coke (AC) was studied to adsorb organic pollutants from coking wastewater. The study initially focused on the sorption kinetics and equilibrium sorption isotherms of AC for the removal of chemical oxygen demand (COD) from coking wastewater. The results showed that when the dose of AC was 200 g L⁻¹, 91.6% of COD and 90% of color could be removed after 6 h of agitation at 40°C. The kinetics of adsorption of COD from coking wastewater onto AC was fit to the pseudo-second order model. The adsorption of COD onto AC was enhanced with an increase of temperature, indicating that the adsorption process would be a chemical adsorption rather than a physical one [91].

Bottom ash, a kind of waste material generated from thermal coal-fired power plants, is generally used in road bases and building materials. Bottom ash was used to remove the organic pollutants in coking wastewater and papermaking wastewater. Particular attention was paid on the effect of bottom ash particle size and dosage on the removal of chemical oxygen demand (COD). The results show that the COD removal efficiencies increase with decreasing particle sizes of bottom ash, and the COD removal efficiency for coking wastewater is much higher than that for papermaking wastewater due to its high percentage of particle organic carbon (POC). Different trends of COD removal efficiency with bottom ash dosage are also observed for coking and papermaking wastewaters because of their various POC concentrations [92].

7.2. Adsorption on clays and clay minerals adsorbents

Several adsorbents were used for the removal of these pollutants. One of an effective and low cost adsorbents is calyx and clay minerals. Natural clay minerals due to their high surface area and molecular sieve structure are very effective sorbents for organic contaminants of cationic or polar in character. Natural and modified clay minerals and zeolites are good

candidates for improving activated carbon(AC) performance, because they have large surface areas for retention of pollutants [93].

Adsorbent prepared from organoclays and activated carbon were shown to remove a variety of organic contaminants [94-95]. Montmorillonite was applied as adsorbent for the removal of cationic surfactants, while the hydrophilic surface of montmorillonite was modified and used as adsorbent [96]. Calcined hydrocalcites was prepared and used to remove organic anionic pesticides [97] from polluted water. Vesicle-clay complexes in which positively charged vesicles composed of didodecyldimethylammonium bromide (DDAB) were adsorbed on montmorillonite and removed efficiently anionic (sulfentrazone, imazaquin) and neutral (alachlor, atrazine) pollutants from water. These complexes (0.5% w:w) removed 92–100% of sulfentrazone, imazaquin and alachlor, and 60% of atrazine from a solution containing 10 mg/L. A synergistic effect on the adsorption of atrazine was observed when all pollutants were present simultaneously (30 mg/L each), its percentage of removal being 85.5. Column filters (18 cm) filled with a mixture of quartz sand and vesicle-clay (100:1, w:w) were tested. For the passage of 1 L (25 pore volumes) of a solution including all the pollutants at 10 mg/L each, removal was complete for sulfentrazone and imazaquin, 94% for alachlor and 53.1% for atrazine, whereas removal was significantly less efficient when using activated carbon. A similar advantage of the vesicle-clay filter was observed for the capacities of removal. Table (4) show the removal efficiencies of organic pollutants from water by DDAB-Clay complex adsorbent [98]

Data in parentheses correspond to the procedure when dried complex was added to the solution, whereas the other case correspond to the removal after incubation with DDAB followed by clay addition.

Data in brackets are the predicted removal by Langmuir equation (binding coefficients)

Zhao et al. [99] prepared mesoporous silica materials and used it for adsorption of organic pollutants in water. Mesoporous silica materials is performed using self-assembling micellar aggregates of two surfactants: cetylpyridinium bromide (CPB) and cetyltrimethylammonium bromide (CTAB). The retention properties have been studied of these two kinds mesoporous silicas towards environmental pollutants (mono-, di-, tri-chloroacetic acid, toluene, naphthalene and methyl orange). The effect of the composition (presence and absence of surfactants, different kinds of surfactants) on the sorption performance has been considered. They found that materials show excellent retention performance toward chloroacetic acids, toluene, naphthalene and methyl orange. The materials without surfactants does not show, if any, affinity for ionic and non-ionic analytes.

The applicability of mesoporous aluminosilica monoliths with three-dimensional structures and aluminum contents with $19 \leq \text{Si/Al} \leq 1$ was studied as effective adsorbents of organic molecules from an aqueous solution. Mesoporous cubic Pm3n aluminosilica monoliths were successfully fabricated using a simple, reproducible, and direct synthesis (scheme 2). The acidity of the monoliths significantly increased with increasing amounts of aluminum species in the silica pore framework walls. The batch adsorption of the organic pollutants onto (10 g/L) aluminosilica monoliths was performed in an aqueous solution at various temperatures. These adsorbents

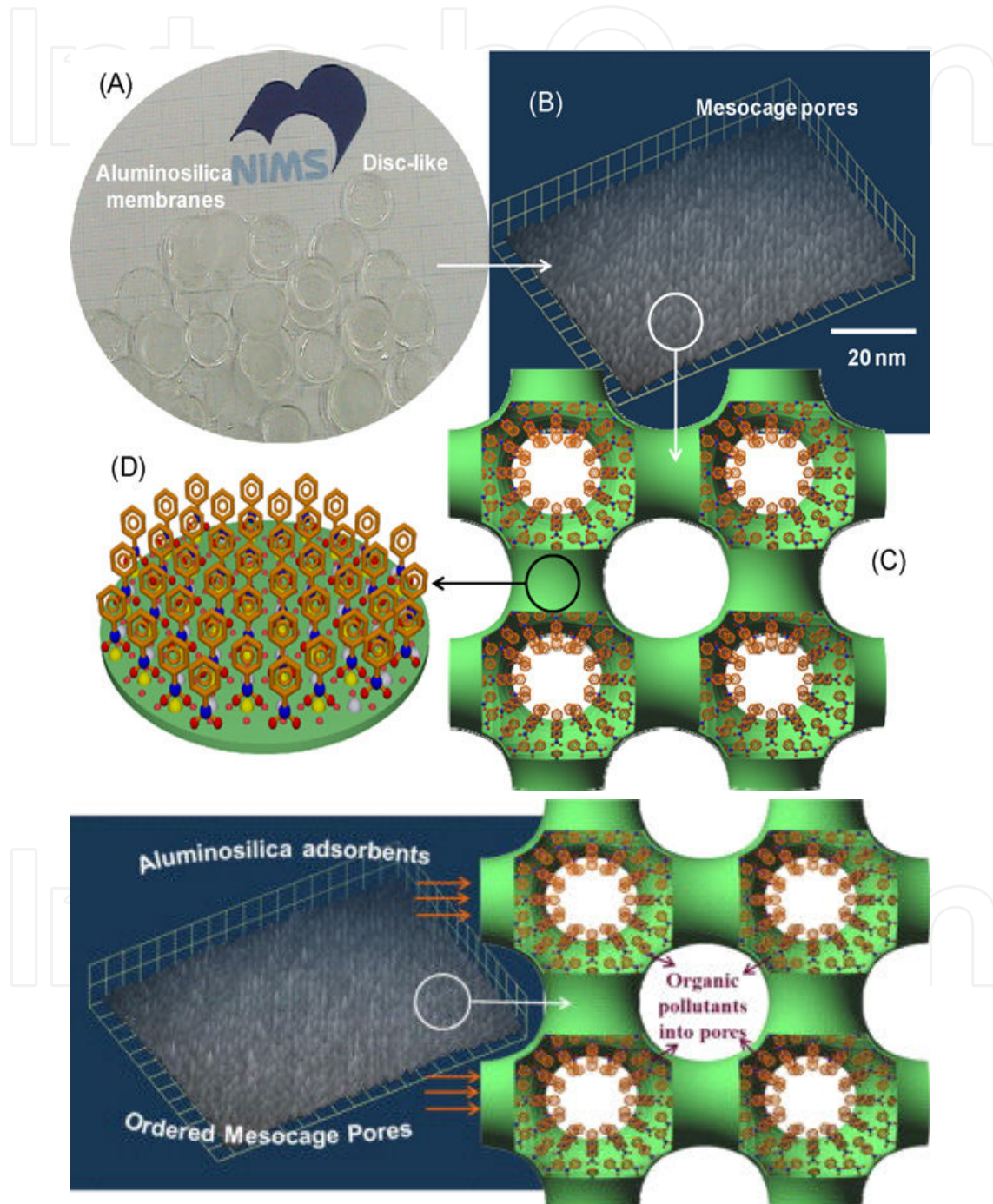
exhibit efficient removal of organic pollutants (e.g., aniline, pchloroaniline, o-aminophenol, and p-nitroaniline) of up to 90% within a short period (in the order of minutes). In terms of proximity adsorption, the functional acid sites and the condensed and rigid monoliths with tunable periodic scaffolds of the cubic mesocages are useful in providing easy-to-use removal assays for organic compounds and reusable adsorbents without any mesostructural damage, even under chemical treatment for a number of repeated cycles [100].

% removal	Initial herbicide conc. (mg/L)	DDAB Conc.(Mm)	Pollutants
37.3±0.3	8	3	Atrazine
(57.4± 0.7)	8	5	
56.6±1.0 (59.8±0.1) [59.0]			
94.9±0.8	10	3	Alachlor
(85.6±1.0)	10	6	
95.5±0.1 (87.2±0.2) [92.7]			
73.6±0.4	10	3	Imazaquin
(92.0±0.3)	10	6	
75.52±0.3 (92.3±1.0) [95.8]			
98.0±1.0	10	3	Sulfentrazone
(99.7±0.1)	10	6	
99.7±0.1			
(99.7±0.1) [99.9]			

Table 4. Removal of organic pollutants from water by DDAB-Clay complex adsorbent ^{a,b} (From Undabeytia et al. [98])

Modified clays were used as adsorbents for the removal of organic pollutants from wastewater. Two pillared clays are synthesized by intercalation of solutions of aluminium and zirconium and evaluated as adsorbents for the removal of Orange II and Methylene Blue from aqueous solutions. The contact time to attain equilibrium for maximum adsorption was found to be 300 min. Both clays were found to have the same adsorption capacity when Orange II was used as adsorbent, whereas the adsorption capacity of Zr-PILC was higher (27 mg/g) than that of Al-PILC (21 mg/g) for Methylene Blue. The adsorption kinetics of dyes has been studied in terms of pseudo-first- and -second-order kinetics, and the Freundlich, Langmuir and Sips isotherm models have also been applied to the equilibrium adsorption data. The addition of NaCl has been found to increase the adsorption capacities of the two

pillared clays for Orange II Pillared InterLayered Clays (PILCs) are porous materials that can be obtained by the intercalation of soils, thereby creating high value added materials from natural solids [101]. Also, pillared clay adsorbent was used for the removal of benzo(a)pyrene and chlorophenols [102], chlorinated phenols from aqueous solution by surfactant-modified pillared clays [103] and herbicide Diuron on pillared clays [104].



Scheme 2. Aluminosilica monoliths with a disc-like shape (A) and mesocage pores (B) as adsorbents (C) of organic compounds (I–IV) inside the mesocage cavity and onto pore surfaces of 3D cubic Pm_{3n} structures (D). Note that 3D TEM image (B) was recorded with aluminosilica monoliths with a Si/Al ratio of 4 (From El-Safty et al. [100]).

8. Conclusion

Organic pollutants in the ecosystem, especially persistent organic pollutants (POPs), are of the most important environmental problems in the world. The literature reviewed revealed that there has been a high increase in production and utilization of organic pollutants in last few decades resulting in a big threat of pollution. Efficient techniques for the removal of highly toxic organic compounds from water and wastewater have drawn significant interest. Adsorption is recognized as an effective and low cost technique for the removal of organic pollutants from water and wastewater, and produce high-quality treated effluent. This chapter highlighted the removal of organic pollutants using adsorption technique with different kinds of natural and synthetic adsorbents.

Many researches have given considerable attention aimed at establishing to the removal efficiency of organic pollutants by adsorption technique. To decrease treatment costs, attempts have been made to find inexpensive alternative activated carbon (AC), from waste materials of industrial, domestic and agricultural activities. Also, clays and natural clay minerals, due to their high surface area and molecular sieve structure, are very effective adsorbents for organic contaminants. The chapter focus, reviews and evaluates literature dedicated on the adsorption phenomenon, different types of natural and synthetic adsorbents, adsorption of dyes, phenols, pesticides and other organic pollutants. Finally it ended with recent researches of organic pollutants adsorption on activated carbons, clays and clay minerals.

Abbreviations

AC Activated carbon, PCP Pentachlorophenol

CAC Commercial Activated carbon, PCDD/Fs polychlorinated dibenzo-p-dioxins and dibenzofurans

PAC powdered activated carbons, DDT dichloro-diphenyl-trichloroethane

ACC Activated carbon cloth adsorbent, DNOC 2,4-dinitrophenol (DNP) and 2-methyl-4,6-dinitrophenol

WC Wood charcoal, HCB Hexachlorobenzene

GAC Granular activated carbon, CD Cyclodextrin

HIC Hemidesmus Indicus carbon, BP Bromopropylate

POPs Persistent organic pollutants, LDHs MgAl layered double hydroxides

BET Brunner, Emmett, and Teller, MTBE Methyl tert-butyl ether

TCP 2,4,6-trichlorophenol, MP Methyl parathion

DCP Dichlorophenol, TCEP Tris (2-chloroethyl) phosphate

BA Bagasse ash, TC Tetracycline

BFD Blast furnace flue dust, DXC Doxycycline-hyclate

TWMP Treated watermelon peels, CTC Chlortetracycline-HCl

PPC Potato peels charcoal, CA Cellulose acetate

WBA Wood-shaving bottom ash, CA-triolein Cellulose acetate (CA) embedded with triolein

CDPs Cyclodextrin-based polymer, EBC Empty-bed contact time

CG Coffee grounds, DDAB Ddidodecyldimethy- lammonium bromide

MS Melon seeds, CPB Cetylpyridinium bromide

OP Orange peels, CTAB Cetyltrimethylammonium bromide

MB Methylene blue, EPA Environmental Protection Agency

RR141 Red Reactive, 141 WHO TheWorld Health Organisation

POPs Persistent organic pollutants, PhAcS Pharmaceutically active substances

OCPs Organochlorine pesticides, PCBs polychlorinated biphenyls

TMP Trimethoprim, PCP Pentachlorophenol

PhAcS Pharmaceutically active substances, PCDD/Fs polychlorinated dibenzo-p-dioxins and dibenzofurans

PCBs polychlorinated biphenyls, DDT Dichloro-diphenyl-trichloroethane

COD Chemical oxygen demand, MW Molecular Weight

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