



Comprehensive Review on the Efficacy of Alkylammonium Cation Pillared Clays for Sorption of Volatile Organic Carbons

Onwuka K.E., Aghalibe C.U., Nkwoada U.T., Igwe J.C., Osigwe C.E., Eze K.S.

Department of Pure and Industrial Chemistry, Abia State University Uturu, Nigeria

Correspondence email: mailkelechi25@gmail.com

Abstract Utilization of adsorption process exhibits versatile applications for wastewater treatments due to its simplicity and lower costs as compared to other traditional technologies. Among the alternative sorbent materials, the use of abundantly available sorbent like clays for adsorption of volatile organic carbons like Benzene, Toluene, Ethylbenzene and Xylene has drawn increasing attention worldwide. Clays, in its natural and modified forms, have been extensively employed for the removal of organic contaminants from different wastewaters. The current review appraises the sorption performance of natural and modified clays for application to environmental clean-up. The adsorption capacity of volatile organic contaminants are comprehensively reviewed. The effect of the experimental conditions (pH, initial concentration (Co), surfactant loading, etc.) on the adsorption capacity is also discussed. Furthermore, Isotherms and Kinetic Models are also appraised. The current review exploits an attempt to draw a prior knowledge about the technical viability of clay sorption process by assessing outcomes of the studies published in the last two decades.

Keywords Mono-aromatic hydrocarbons, clays, alkylammonium cation, adsorption, isotherm

1. Introduction

Mono-aromatic hydrocarbons – benzene, toluene, ethylbenzene and xylenes (BTEX) – are common pollutants found in groundwater plumes and in other water resources, as a result of the disposal of contaminated industrial effluents and accidental events such as oil spills and oil pipeline leakages [1-4]. Water is a vital resource for life but is increasingly being polluted by anthropogenic activities including oil spillage, urbanization, population growth, poor land use, and agricultural activities that have lead to rapid degradation of surface and ground water quality. Of these, oil spillage remains a serious concern especially in oil producing regions of the world. Regulations [5] have done much to prevent oil contamination of water. Egwaikhide [6] reported that yearly, both the government and various multi-national private oil companies contend with hazards of crude oil spillage which affected both aquatic and terrestrial ecosystems.

Most oil spills occur due to underground water well blowouts, tanker accidents, storage tank failures, production platform blowouts, intensified petroleum exploration on the continental shelf, transfer operations between ships and shores, economic sabotage and youth restiveness like the Niger Delta militias in South-South, Nigeria.

The negative health effects that result from the consumption of these compounds include cancer, liver lesions, drowsiness and irritation of organs [7]. Mitra and Roy [8] further reported that human exposure to BTEX compounds over a long period of time results in skin and sensory irritation, adverse respiratory health effects and

central nervous system irritation. In spite of the negative effects they pose to human health, BTEX compounds remain overlooked and untreated in municipal systems, thereby increasing the risk of water-related diseases through their ingestion.

Recent remediation efforts have focused mainly on the compounds contained in heavy oil fractions, i.e., the poly-aromatic hydrocarbons (PAHs) which are known to cause conspicuous environmental degradation, and are more noticeable at pollution sites [9]. BTEX compounds on the other hand are often overlooked in remediation efforts due to their obscure nature in water. Although their presence in water may not be as easily discernible as with PAHs, BTEX compounds are more abundant in the environment and can be found in a variety of sources [34,74,75], some of which include petrochemical industry waste streams, household wastes and municipal landfills [71], as well as groundwater plumes, especially when located at a considerable distance from an oil spill site [19,25]. In addition, studies such as Grady and Casey [36], Schmidt [64], Mitra and Roy [8], and Reddy [63] have reported the presence of BTEX compounds in drinking water, indicating extensive health risks that may not be immediately evident. Zhang [7] have also highlighted the persistent presence of BTEX compounds in air, and have reported the transportation of these compounds from air into water bodies as a result of rainfall. As a result, it is imperative that the remediation of these compounds in water is prioritized in future water treatment systems.

Various methods have been reported for BTEX removal from aqueous solutions [14,15,53,54,80]. However, adsorption processes have been shown to offer a more efficient way to remove pollutants in wastewater before discharge into the environment. Organoclays, essentially 2:1 clays, have been widely used for the removal of BTEX compounds from aqueous solutions [14,15,42,54,67].

1.1. Properties of BTEX Compounds

Benzene, toluene, ethylbenzene and xylenes are mono-aromatic ring compounds with a 6-carbon benzene ring as their core structure. Due to their closed structures, these compounds, especially benzene, are generally considered to be non-reactive species [95]. However, it is well-known that these compounds have the ability to undergo hydrogenation and certain substitution reactions. At oil-spill sites, BTEX compounds can be transported through several metres under favourable redox conditions causing them to be persistent pollutants in both soil and water [96,97]. Their ability to dissolve in water, relative to their poly-aromatic counterparts, is due to low octanol-water partition coefficient (K_{ow}) values [98,99] which favour hydrophilic dissolution, in spite of their hydrophobic nature. Furthermore, BTEX compounds are mostly found to coexist with one another or with methyl tert-butyl ether (MTBE) – a common fuel oxygenate reported to be a common organic pollutant in water. The co existence of BTEX compounds with one another suggests that their toxicity is amplified through their interactions with one another; however, such interaction models have not been verified [14,84]. Interestingly, BTEX compounds are among the most abundantly produced chemicals in the world, in spite of their ill effects on human health and resultant environmental degradation [22]. They are utilized as solvents in many industrial processes, as well as used in many household products including insecticides and paints [100].

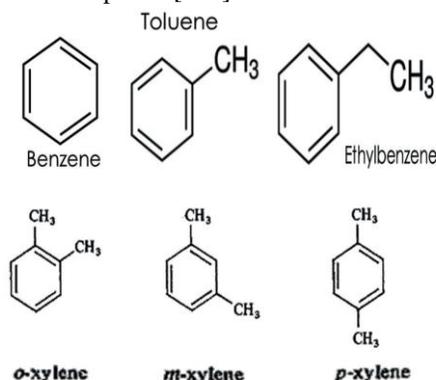


Figure 1: Structures of BTEX Compounds



1.2. Sources and Reported Concentrations of BTEX compounds in Water

BTEX compounds are priority pollutants according to the United States Environmental Protection Agency (US EPA) [101]. These volatile organic compounds (VOCs) are often present in air, especially in areas where oil spillages have occurred [11,12,102], and in closely-located groundwater plumes. They are also found to be dissolved in high concentrations in oilfield produced water –and oil and gas industry effluent [103]. Industries that utilize petrochemicals for the production of paints, adhesives, inks and rubber also produce BTEX compounds in their effluents, although extensive studies have not been conducted to identify BTEX compounds in these effluent streams or characterize their concentrations [2]. BTEX compounds are more abundant in the environment than their poly-aromatic counterparts. They are present in either gaseous or liquid media in the environment, and their presence has been reported in a number of studies. Most commonly reported is the detection of these compounds in groundwater as a result of oil spills and oil pipeline leakages. Mitra and Roy [8] reported that the main source of BTEX contamination in water is the release of petroleum products ranging from gasoline and diesel fuel to heating oil from leaking oil tanks.

Meniconi [104] characterized the composition of hydrocarbons and other compounds released into water in different regions of Brazil as a result of oil spills. The study reported that the concentration and persistence of BTEX compounds was directly proportional to the scale and duration of the oil spill, highlighting high BTEX concentrations in large-scale, long duration oil spills. Lu [105] reported the migration and dissolution of BTEX compounds in groundwater due to a leak at a petroleum oil facility. Camili [97] tracked the hydrocarbon transport at the site of the *Deepwater Horizon* oil spill and reported that a continuous and persistent plume of oil, more than 35 km in length (at a depth greater than 1 100 m from the surface of the water) was present. Samples obtained from this oil plume contained high concentrations of mono-aromatic compounds, including BTEX compounds. Wang *et al* [81] characterized near-surface groundwater (0 – 5 m), and deeper-level groundwater (15 – 60 m), and reported BTEX concentrations of 155 µg/kg of water, and 2.6 µg/kg of water, respectively. This report showed that in spite of the depth of groundwater, BTEX compounds were still present, albeit at low concentrations. Reddy *et al* [63] examined the composition and fate of oil and gas that flowed from the Macondo well during the *Deepwater Horizon* oil spill. The study highlighted that the most abundant hydrocarbons present in the water were BTEX compounds (up to 78 µg/L). These findings have been reiterated in various studies, such as Essaid *et al* [106], Margesin *et al* [107], and Das and Chandran [108].

The persistence of BTEX compounds in groundwater plumes is worrisome, especially in vulnerable regions like Africa and South-East Asia where the direct reliance on groundwater in the form of drinking wells and boreholes for potable and other uses is high [61]. The health risks posed as a result of such chemical persistence cannot be overstated. In addition to groundwater, other water sources, including industrial effluents and drinking water, have been investigated for the presence of BTEX compounds [64]. In industrial effluents, BTEX compounds are undeniably present, especially in the effluents of industries that utilize one or more of the BTEX compounds as solvents for their processes. The most commonly reported source of BTEX in terms of industrial effluents is oilfield-produced water – an oil and gas effluent that is usually discharged into coastal bodies and other surface water bodies, in regions where environmental regulations are not well-enforced. Ranck *et al* [109] reported the presence of BTEX compounds in produced water at high concentrations. Dorea *et al* [110] reported concentrations of BTEX compounds in produced water obtained from Brazil ranged from 96.7 to 1 397 µg/L. The values reported in [110] flirt rather closely with the acceptable limits for these compounds (1.0 mg/L for benzene, 1.3 mg/L for toluene, 1.0 mg/L for ethylbenzene and 1.4 mg/L for xylenes) according to Australia's Water Corporation (Australian [95]). It can be estimated from the reported concentrations of these compounds in produced water that the concentrations of these compounds are very often exceeded in other industrial effluents from petrochemical, inks and adhesives, as well as rubber industries, though there are no studies reported in this regard [85,95].

Still, the health risks posed to human health through the ingestion of these compounds, considering benzene is a confirmed carcinogenic, cannot by any means be exaggerated. Remarkably, household hazardous wastes have also been reported to contain high concentrations of BTEX compounds. Ro *et al* [111] revealed that household products such as garden pesticides, pharmaceuticals, paints, some detergents and personal care products contain BTEX



compounds, hence resulting in an increase in the concentration of these compounds in municipal waste streams. Chiriac *et al* [112] also reported the presence of BTEX compounds in municipal solid wastes. A study by Robinson *et al* [113] highlighted the high pollution potential of trace organic compounds such as BTEX compounds in household wastes that are disposed in landfills.

These compounds can readily dissolve in water and be carried in run-off to surface water bodies, thus posing major risks to water resource health, marine life and subsequently human health. From the above it is evident that BTEX compounds can easily be encountered in the environment. Although reported concentrations in treated drinking water may seem low, the bioaccumulation effect cannot be ruled out, nor can the subsequent health effects that may result. The presence of these compounds in groundwater plumes, and their ability to persistently be transported to great depths in groundwater, increases the risks of water-related illnesses and deaths in highly vulnerable regions like some parts of Africa and South-East Asia, where municipal treatment systems do not exist and residents rely solely on groundwater for all their needs.

2.0 Natural Clay

Fuller's earth has long been used industrially for its decolorising properties all the world over and it is an inexpensive and readily available mineral. McKay *et al* [114] reported the adsorption capacity of Fuller's earth for basic and Acid Blue to be 220 and 120 mg g⁻¹, respectively. Thus, they proposed this adsorbent for the treatment of textile effluents. The adsorption capabilities of clay were due to the negative charge on the structure of fine grain silicate minerals [72,82]. This negative charge was neutralized by the adsorption of positively charged cations such as dyes etc. Besides, the clays possessed large surface area ranging up to 800 m² g⁻¹, which contributes to its high adsorption capacity [115]. There are many types of clays but montmorillonite clays are expected to have the highest sorptive capacity in comparison to other. El-Guendi [116] proposed a three step model for the adsorption of cationic dyestuffs (Basic Blue 69 and Basic Red 22) from aqueous solutions on to natural clay. In another study, El-Guendi [116] studied the adsorption of cationic dyestuffs (Basic Blue 69 and Basic Red 22) from aqueous solutions by natural and activated clays. The maximum adsorption capacities (q_{max}) of basic blue (BB 69) and basic red (BR 22) on to natural clay were 390 mg g⁻¹ and 365 mg g⁻¹, respectively. The natural clay was treated with H₂O₂ and HCl to enhance its adsorption capacity for dyestuffs. The efficiency of activation with H₂O₂ was greater by 23% and 13% in the case of BB 69 and BR 22, respectively, when compared to natural clay. The efficiency of activation with HCl was greater by 30 and 16% in the case of BB 69 and BR 22, respectively relative to natural clay.

2.1. Active sites on clay surface

On clay mineral surfaces, active sites are a very important concept, because they determine the chemical reactions that applicable to the clay [117]. These active sites or surface functional groups are defined by the geometric arrangement of surface atoms of clays and their chemical composition. They can be described on the basis of their location (edge or basal surface), geometric arrangement of surface atoms, chemical composition, and accessibility. Generally speaking, there are six kinds of active sites which are important for explaining interactions of organic molecules to the clay surfaces. They are isomorphic substitution sites, hydrophobic sites, broken edge sites, neutral siloxane surface, metal cations occupying cation exchange sites and water molecules surrounding the exchangeable cations [23, 33, 43, 117]. Among the active sites, the first four sites are more important for explaining clays to be developed as sorbents. Firstly, isomorphic substitution within the tetrahedral and/or octahedral sheets can generate negative charge on the layers. It is usually balanced by hydrated exchangeable cations in the interlayer (mostly Ca²⁺, Mg²⁺ and Na⁺). The extent of hydration varies greatly and depends on many factors related to the nature of interlayer cations and composition of the layers [118]. Isomorphic substitution can create a kind of active site in the clay lattice of 2:1 layer silicates. This phenomenon happens on the basal surfaces of charged 2:1 layers silicates including smectites which include montmorillonite, hectorite, vermiculites and micas. In addition, isomorphic substitution can occur in either the octahedral or tetrahedral sheet and many clay minerals are characterized by varying degrees of substitution in both sheets [119]. As for sorption of polar and charged organic materials, the location of isomorphic



substitution sites in 2:1 layer silicates for example on octahedral or on tetrahedral will have a great impact [117]. The extent and type of isomorphous substitution occurring in layered silicates can strongly influence the selectivity for inorganic and organic cations, degree of swelling and accessibility of the interlamellar region. Although the siloxane surface is considered unreactive due to the strong bond between the Si and O atoms, substitution of Si by Al increases the reactivity and surface acidity. Yunfei [117] suggested that repulsion between non-bonding electron pairs on the surface oxygen atoms increases due to Al substitution and that the overall basic strength of the oxygen plane increases. As the extent of Al for Si substitution increases, the potential for polar organic molecules to hydrogen bond directly to the clay surface increase [120].

Secondly, hydrophobic site is also one of the active sites. Sorption of organic molecules on clay surfaces can impart a hydrophobic nature to the clay surface [90,117]. The most common example is the cation exchange of inorganic cations, usually alkyl ammonium cations on montmorillonite. Smectite surfaces have a high selectivity for organic cations such as hexadecyltrimethylammonium (HDTMA) cations. The modified organo-clays have significantly different surface properties than the original unmodified clay. The presence of the organic cations between the layers can serve as molecular pillars which allow organic solutes to be adsorbed (or absorbed) by the organo-clay. The imparted hydrophobic property of the modified clay surface makes organo-clays efficient sorbents for non-polar organic compounds [117].

Thirdly, the edges of the particles which bear broken-end hydroxyls such as Si-OH and Al-OH (or Mg-OH) are also very important sites for adsorbing [121]. They are dependant on pH value as they become protonated or deprotonated according to the pH value of the solution [117]. At low pH, these sites will develop a positive charge due to the adsorption of protons, so organic acids and oxyanions can interact with these positive charged sites strongly. With the increase of the pH, these sites will develop a neutral charge sites and finally will develop a negative charge when taken to very high pH. At the same time, the contribution of these edge sites to the cation exchange capacity (CEC) depends on the size and shape of the clay particles. If the particles are large, the CEC from these sites are minimal. When the particles become small, the contribution of them will become large. In some cases, an organic molecule does not replace the exchangeable metal cation, but coordinates directly to the metal cations which occupy the exchangeable cation sites. Phenol for example, can interact with exchangeable alkali and alkaline earth metal cations which occupy cation exchange sites [122].

In addition, the neutral siloxane surface which is considered to have a predominantly hydrophobic character [21] due to strong bond formed between the Si and O atoms, the siloxane surface on clay minerals is unreactive [123]. This surface has interesting sorption properties and is capable of polarizing water molecules surrounding the exchangeable cations. The uncoordinated surface atoms which can donate protons to adjacent organic solutes [124] are also important active sites for clay minerals. In general, the origins of charges on the clay mineral lattice are believed to be mainly because of isomorphous substitution, lattice imperfections, broken bonds at the edges of the particles, and exposed structural hydroxyls etc [117].

2.2. Organo-clay

Clay minerals consist of small crystalline particles with silica-oxygen tetrahedral sheets and aluminium or magnesium octahedral sheet, where an aluminium or magnesium ion is octahedrally coordinated to six oxygens or hydroxyls [74,75,84,85]. Because of isomorphous substitution of silicon ion by aluminium ion in the tetrahedral layers or similar substitution of aluminium ion by magnesium ion, smectite minerals have a net negative charged. Thus, cations like sodium, potassium and calcium may be attracted to the mineral surface to neutralize the layer charge. Organo-clays are synthesized by grafting cationic surfactants [124] (Such a quaternary ammonium compounds $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR']^+$ where R and R' are alkyl or aromatic hydrocarbons etc.) onto clay minerals. The interlaminar distance of the d001 plane of the clay which has not been organically modified, is relatively small, and the interlayer environment is hydrophilic. Intercalation of organic surfactant between layers of clays not only changes them from hydrophilic to hydrophobic, but also greatly increases the basal spacing of the layers. The increased basal spacing together with hydrophobic surface makes organo-clays an effective material for



adsorbing oil spills on roads [117].

2.3. Cation exchange mechanism

Because of isomorphous substitution of lower valence cations such as Al^{3+} substituting Si^{4+} in the tetrahedral sheets or Mg^{2+} replacing Al^{3+} in the octahedral sheets, 2:1 phyllosilicates usually contains a deficit of positive charge, so they have net negative charge. In nature, the negative structural charge is balanced by exchangeable cations such as Na^+ , Ca^{2+} etc. at the aluminosilicate surfaces. Cation exchange reaction starts at the edges of clay particle and then spreads toward the centre in a highly regular fashion. Kinetic studies have been undertaken by [125], which show that when the temperature increases the reaction rate will increase. Secondly, this study has shown that the clay minerals' chemical and structural characteristics have profound influences on the rate of cation exchange reactions. The charge on the clay layers and its location (octahedral or tetrahedral) will influence the strength of the electrostatic attraction between layers and mobility of interlayer space. At the same time, reaction rates are influenced by the size and valence of the exchanging inorganic cations [117]. When highly charged silicates are saturated with larger, less hydrated, monovalent cations such as K^+ , Rb^+ , NH_4^+ , Cs^+ , the attraction between layers is greatest. When the layers are saturated with Na^+ , Li^+ , Ca^{2+} , Mg^{2+} which have larger hydration energies, then the attraction between the layers will be overcome and the basal spacing will be increased even complete dissociation can occur small highly hydrated cations are more mobile and easier to replace since inorganic cations have relatively high hydration energies and usually several layers of water molecules will be associated with them. These clay surface have a predominantly hydrophilic character which makes them ineffective sorbents for hydrophobic organic contaminants. This is a direct result of the presence of hydrated cations near the clay surface.

When hydrophobic modification of clay mineral's surface is undertaken, a variety of organo-clays can be formed. An important consequence of replacing inorganic cations with organic cations is that the clay surface will take on a hydrophobic character instead of hydrophilic [126]. Usually, active sorption sites on clay surfaces such as isomorphous substitution sites, neutral siloxane surface, broken edge sites are important for explaining the sorption. Because of electrostatic and non-coulombic forces, organic cations are attached on 2:1 layer silicate surfaces. In this process, the Gibbs free energy for the cation exchange reaction on clays increase as the chain length of the alkyl chains increased. This was first reported by Jouary and Chassin [127]. The additional stabilization energy gained with increasing chain length is attributed to van der waals interactions between the alkyl chains and clay surface. On the other hand, in terms of active sites, the alkyl ammonium cations are stabilized by electrostatic interaction of the protonated amine with isomorphous substitution and broken edge sites via ion exchange and through van der waals interactions of the hydrophobic portion of the organic cation (i.e., alkyl chains) with the neutral portion of the siloxane surface. But if the molecules are too large, steric hindrance will limit the amount sorbed when the organic cations become too large to fit in the interlamellar region. This occurs when the projected surface area of the organic cation approaches the charge density of the clay mineral [128]. Except steric effects, the charge density of the clay will influence the accessibility of interlamellar sorption sites. In general, if the organic cation has a diameter of less than 6\AA as its smallest dimension, it can participate in most ion exchange reactions. The size of the clay particles, type of exchange cations, total layer charge and the type of isomorphous substitution (i.e., tetrahedral vs. octahedral) have all been known to influence the interaction of organic cations with 2:1 layer silicates [128].

The arrangement of the intercalated organic cations in the interlamellar region depends strongly on the size and shape of the organic cations as well as the charge density of the clay. Using infrared spectroscopy, Yunfei [117] observed that if the layer charge is low, then the preferred orientation of the organic cations in the interlayer region is parallel to the silicate layer. With the increasing of charge density, however, the organic cations are oriented nearly perpendicular to the clay layers. The orientation of the alkyl ammonium cations in the interlayer region has a large influence on the hydrophobic properties of the modified clay.

In addition, the concentration of organic cations sorbed usually can reach as much as cation exchange capacity (CEC) of clays. Some authors have however reported that the organic cations are generally sorbed on charged 2:1 layer silicates in excess of the cation exchange capacity (CEC) of the clay [117]. When organic cations replace



hydrated inorganic cations, the silicate surface is changed from hydrophilic to hydrophobic, the organic cations can adhere to isomorphic substitution sites via electrostatic interactions or they can adhere to the sorbed organic cations by van der Waals forces [129]. If they are bonded to sorbed organic cations by van der Waals forces then the sorbed organic cations will increase even exceed the cation exchange capacity (CEC) of the clay; For example, Jaynes *et al* [126] reported hexadecyltrimethylammonium (HDTMA) sorption at 150% of the cation exchange capacity on montmorillonite. A similar sorption which is excess the CEC was reported by Rytwo *et al* [130] on montmorillonite. Depending upon the size of the alkyl substituent on the organic cations and the nature of their interaction with neutral hydrophobic compounds, there are two classes of organic clays to satisfy different requirements. One is adsorptive clays while the other is organophilic clays [20,39,48,117].

2.4. The difference of sorption behaviour between two organo-clays

The sorption behaviors of hydrophobic compounds on short chained quarternary ammonium cation modified clays (adsorptive clays) and long chained organic cation exchanged clays (hydrophobic clays) are very different. In larger organic cations such as HDTMA, the organic cations are anchored to the clay surface by electrostatic forces between the positive charge on the organic cation and isomorphic substitution sites on the surface of clay. The long hydrophobic alkyl chain of the organic clays can interact with each other to create a hydrophobic or organophilic phase which functions as a partitioning medium. As for small organic cations such as TMA and TMPA, they have no long alkyl chains which can interact with each other, so at maximum adsorption on smectite clays, they are discrete entities on the siloxane surface of smectites and are arranged in monolayers, hence they do not form a partition phase as that exist in the organophilic clays [117].

2.5 Arrangement of organic cations in the organo-clays

The arrangement of organic cations in organo-clays depends on the size of organic cation, for instance the length of alkyl chain and layer charge of the clay minerals [128]. Generally speaking, in adsorptive clays, the organic cations only form monolayers. In the case of organophilic clays, the organic cations may form monolayers, bilayers, pseudotrimolecular layers or paraffin complexes [117]. These three arrangements of organic cations also affects the basal spacing of organic clays which can be analysed by XRD. For example, in the case of HDTMA, the C-16 alkyl chain may form from monolayers to paraffin complexes which correspond basal spacing of d_{001} are 13.7Å, 17.7Å, 21.7Å and >22Å. Different interlamellar arrangements of alkylammonium ions are as follows [30,49,70]:

Monolayers: When the packing density of the chains is low, the chains are assumed an arrangement with the C-C-C plane parallel to the layers, i.e. the chains will lie parallel to the silicate layers. The characteristics basal spacing is 13.6 Å. This spacing is often observed for short alkylammonium ions ($n < 8$).
 Bilayer: chains parallel to the silicate layer. Typical basal spacing is 17.6 Å
 Pseudotrimolecular layers: The polar end groups of the alkylammonium ions remain attached to the layers. By formation of kinks the unpolar chain ends are shifted one above the other and the interlayer separation is determined by the thickness of three alkyl chains. The basal spacing is about 22 Å.
 Paraffin-type layers: The ammonium groups remain attached to the silicate layer, the chains in all-trans conformation point away from the surface. As the orientation of the methyl end group is different for $n = \text{even}$ and $n = \text{odd}$, the basal spacings increase stepwise (alternating spacings) [126]. The theoretical spacings are ($\varphi =$ angle of tilt):

$$n = \text{even: } dL = 11.3 + 1.27 n \sin\varphi$$

$$n = \text{odd: } dL = 11.3 + 1.27 n \sin\varphi + 0.88 \cos\varphi$$

These four types of arrangements are shown in figure 2.



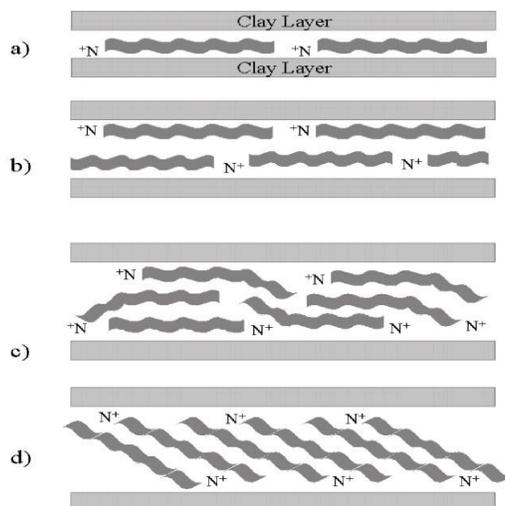


Figure 2: Four types of arrangements

a) Monolayer (about 1.37 nm), b) Bilayers (about 1.77 nm), c) Pseudotrimolecular layer (about 2.17 nm), d) Paraffin complex (>2.2 nm) [125].

2.6. Clay Modification Methods

2.6.1. Thermal treatment

The use of thermal treatment has been recognized as one route to enhance the adsorptive characteristics of raw clays [10]. Whereby the microstructure of the clay (the octahedral sheet), cation exchange capacity, and clay wettability can be changed to enhance the adsorption capacity [94]. Yu *et al* [91] reported a significant increase in the adsorption capacity of pesticide (dicamba) onto calcined anionic clays (Layered double hydroxides (LDHs)). Whilst the untreated LDHs had no affinity for dicamba, the calcined clay showed S-type adsorption isotherm with a rapid adsorption process (reached the equilibrium in 30 min). The adsorption mechanism was based on combined electrostatic attraction and hydrophobicity. In another study, Abdelrahman [10] investigated the combined surface modification and thermal treatment of vermiculites for sulfamethoxazole removal from water. The adsorption experiments revealed that combined thermal pretreatment and surface modification of the clay resulted in higher SMX removal (98%), cf. 95% for single step surface modification. Bamidele [58] investigated the structural properties and adsorption capability of thermally treated kaolinite-biomass composites. Although the specific surface area of the calcined kaolinite-biomass composite was reduced after the thermal treatment, a significant increase was observed in the cation exchange capacities after the calcination at 300 °C. Which resulted in 52–250% enhancement in the amount of 2,4,6-trichlorophenol adsorbed onto the calcined composite. In fact, the effectiveness of the thermal treatment depends on the nature of the adsorbates and the adsorption mechanism [10].

2.6.2. Acid activation

Acids such as HCl, NH₄Cl, and H₂SO₄ have been used to remove mineral impurities and aggregate the clay, which increases the specific surface area. Yu [91] demonstrated the use of aqueous ammonium chloride to activate Algerian clay. The resultant acid activated clay was used for the removal of phenol from industrial wastewater (e.g. textile). The adsorption experiments showed a significant increase (~160%) in the specific surface and the adsorption capacity enhanced to 48.8 mg/g at an initial concentration of 400 mg/L. In another study, Safoora [51] compared the adsorption capacity of phenol onto acid modified and surfactant (HDTMA) modified clays. A 40% higher specific surface area (SSA) was observed for bentonite activated with HCl, as compared to HDTMA modified bentonite. Due to the larger SSA, an order-of-magnitude higher phenol removal was reported for HCl activated clay. In another study [46], the adsorption capacity of HCl activated clay for 2,4,6-trichlorophenol was



also reported as a function of pH, contact time and temperature. However, Schouten [65] showed that although the surface area of activated bentonite (with H₂SO₄) was ~2 times higher than untreated clay and the total pore volume increased from 0.9095 to 0.505 cm³/g, the activated bentonite showed negligible improvement in the adsorption capacity of linear alkyl benzene sulfonate (LAS) due to the acidic (negatively charged) surface which had no affinity to interact with the LAS molecules.

2.6.3. Ion exchange

Ion exchange has been widely used to produce intercalated clays by exchanging the inorganic cations of the clays with either metal/transition metals or organic cations (surfactants). Whilst the latter has been widely acknowledged as the most commonly used method and has been demonstrated for the removal of various organic pollutants, a limited number of studies have been reported for the use of transition metal complexes and metal species for the removal of phenol and phenolic compounds [10]. Zeng [93] found that polymeric Fe/Al metal exchanged bentonite had lower adsorption affinity toward phenol, compared with HDTMA modified clays.

2.6.4. Cationic surfactants

The adsorption capability of raw clays can be improved by exchanging its interlayer inorganic cations (e.g. Na⁺, K⁺, Ca²⁺) with Quaternary ammonium cations (QACs). The enhanced adsorption properties of the resultant organo-clays are caused by both the hydrophobic surface property as well as the expanded interlayer spacing of swelling clays. The organic cations employed to modify natural clays are generally categorized into either (a) organic surfactants with benzyl, phenyl, and/or short-chain alkyl groups such as tetramethylammonium (TMA), trimethylphenylammonium (TMPA), and benzyltriethylammonium (BTEA), or (b) Cationic surfactants with one or more long-chain alkyl groups such as hexadecyltrimethylammonium (HDTMA), cetyltrimethylammonium (CTMA), and didodecyltrimethylammonium (DDDMA) [10]. The use of cationic surfactants such as Gemini surfactants, and natural amine, have been reported for the removal of pesticides and phenolic compounds [29]. Gemini surfactants are kind of surfactants that comprise both aromatic rings and alkyl chain. Clays modified with such surfactants have the benefit of surface hydrophobicity as well as the special π - π interactions with the adsorbate. Clays intercalated with Gemini surfactants demonstrated high adsorption affinity for organic pollutants [10,59,68]. According to the length of the organic cations, the uptake mechanism of the organic contaminants by organoclays has been based on either physical/surface adsorption (driven by van der Waals forces) or partitioning between phases.

Moreover, it has been reported that the longer the modifier alkyl chain (e.g. DDDMA), the more hydrophobic partition medium, and thus the higher adsorption capacity [88]. The adsorption properties of organic- intercalated clays are significantly affected by the chemical structures and molecular arrangements of the organic modifier, as well as the layer charge density of the organoclays [47]. Yu [91] has claimed that compared to low-charge smectite, HDTMA intercalated clays with high-charge density have a higher adsorption affinity towards phenol due to the increased nonpolar interactions with the adsorbates. On the other hand, for the use of small cation chain modifier (TMA, and BTMA) higher adsorption capacities were recorded for organoclays prepared at lower charge density. Whilst the adsorption of aromatic compounds (phenol, benzene, and toluene) onto clays intercalated with small organic cations (BTMA, TMA) usually results in higher adsorption capacity [27].

Moreover, compared to TMA, surfactants with benzyl chain (e.g BTMA) has higher adsorption affinity toward aromatic molecules due to π - π interactions between the benzene ring of BTMA and the aromatic rings of the adsorbate [69]. The adsorption capacity is not only dependent on the type and size of the organic modifier but also on the structure of the organic molecules. Zhongxin [50] found that montmorillonite modified with hexamethylene bispyridinium dibromides (HMBP) exhibited the highest adsorption capacity for phenol among other phenol derivatives (chlorophenol and nitrophenol). Which was attributed to the π - π polar interaction between the pyridine ring and benzene ring in phenols. Therefore, special functional groups within the chemical structure of the organic surfactant control the affinity for specific pollutant molecules and one possible route to enhance the removal of a specific organic molecule is to use a specific modifier having a special functional group [10].



2.7. Adsorptive characteristics of surfactant modified clays

Discrepancies in the adsorption capacity of modified clays were reported for the removal of similar organic adsorbates across the different studies which is attributed to the differences in either the preparation process (including organic matter removal, cationic exchange capacity (CEC)/ surfactant loading, and the properties of the natural clay used to be modified), or the experimental conditions (solution pH, temperature, initial concentration, adsorbent dosage, and contact time). Across different reported studies [10,48,56,66], the general trends of these factors for data sets within a specific study can be explained as the follows:

(a) Surfactant loading (% CEC): the amount of surfactant loading is found to have a significant effect on the degree of the adsorption [16,17]. Generally, the adsorption capacity increases with the surfactant loading (usually expressed as (% CEC) due to either the stronger Van der Waals interactions between the adsorbate and the modified clay surface or increased partitioning effect at higher loading [60]. Nonetheless, it was demonstrated that the rate of change decreasing towards a plateau after which the adsorption capacity was observed to decline with a further increase in the surfactant loading, as other factors become mass-transfer limiting at higher surfactant concentration [95]. Moreover, the rate of change in the adsorption capacity is also controlled by the number of the alky groups of the surfactant [68,76,77,81,86].

(b) pH: The adsorption process on modified clays is significantly influenced by the solution pH. The extent of the pH influence on the adsorption capacity is controlled by the clay surface charge and the ionic (anionic, cationic, or neutral) form of the organic adsorbates [7]. pH is known to control the dissociation of the organic adsorbate, with organic molecules being an anion, cation or neutral at different pH. Whilst the adsorption capacity remains unaffected by pH for neutral molecules, the adsorption dramatically declines in the range of pH when the organic compound deprotonated to anionic form due to the repulsive electrostatic interactions between the anion adsorbate and the negatively charged clay surface.

However, it has been claimed that as the surfactant concentration loading increases the adsorption capacity becomes less influenced by pH [62]. Moreover, Yuri [91], reported that the degree of the pH effect is dependent on the size of organic cations (molecular weight of the surfactant), as the clay intercalated with larger surfactants (e.g. DDDMA) develops more positively charged surface and attracts imazaquin (in its anionic form) at low pH.

(c) Adsorbent dosage: the effect of the adsorbent dosage on the removal efficacy of chlorophenol was investigated by Zhang and his coworker [7], where dodecyltrimethylammonium bromide (DTAB) and (CTAB) were used to modify MMt. Whilst the adsorption amount onto the unmodified clay (MMt) remained unaffected by the increase in the adsorbent dosage the removal of chlorophenol steadily increased for the modified clays due to the more vacant sites being available to adsorb the organic molecules. Similar findings were observed by others for the removal of phenolic compounds [31]. However, Jaynes [42], reported that the adsorption capacity of phenol and phenolic derivatives decreased when the adsorbent dosage increased.

(d) Contact time: the required contact time to achieve a target removal amount of the organic pollutants is of economic importance for the real-world applications. It has been widely acknowledged that the adsorption process starts to increase sharply for a short time period till the equilibrium concentration is reached then a considerable decline is observed for the adsorption amount, as the repulsive electrostatic interactions between the occupied adsorption sites and the adsorbates increases [26,31, 37].

(e) Initial concentration: The trend of the equilibrium uptake increases with the initial concentration of the organic solution as a direct result of the increased driving force (concentration gradient between the bulk solution and the clay surface). Nonetheless, and simultaneously the %organic removal declines [31].

2.8. Adsorption Kinetics

Many attempts have been made to formulate a general expression describing the kinetics of sorption on solid surfaces for liquid-solid phase sorption systems. Existing kinetic models in the literature are easily grouped into two: empirical models and mechanistic models [131].



2.8.1. Empirical Models (Global Rate Models)

The sorption of organic compounds, such as (BTEX), onto natural sorbents has been described on a molecular level as a complex process by models which involve complicated mathematical computations [78]. Thus, attempts at simplification have been considered on a macroscopic scale for practicality and ease of understanding the mechanism of sorption and potential rate controlling steps such as mass transport and chemical reaction processes. From a macroscopic point of view, three global kinetic rate models are often used in the literature: pseudo-first-order kinetics; pseudo-second-order kinetics and the Elovich model.

2.8.1.1. Pseudo-first-order

The pseudo-first-order equation was first represented by Lagergren for the sorption of oxalic acid and malonic acid onto charcoal [44]. The model is generally expressed

$$\text{as: } \frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2.1)$$

where q_e and q_t are the sorption capacity at equilibrium and at time t , respectively (mgg^{-1}) and k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). After integration and applying the boundary conditions $q_t = 0$ at $t = 0$ and q_t at $t = t$, equation (2.1) yields:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (2.2)$$

The rate constant is obtained by a linear regression analysis of the $\log(q_e - q_t) = f(t)$ function in equation 2.2 above. Ho and McKay [114] observed that in most cases in the literature, the pseudo-first-order equation of Lagergren [44] does not fit well for the whole range of contact time, and is generally applicable over the initial 20 to 30 minutes of the sorption process.

2.8.1.2. Pseudo-second-order

Chang *et al* [17], Valderrama *et al* [78], Anirudhan [24], Nourmoradi *et al* [54] and Chidi *et al* [55] are some examples of researchers who have used the pseudo-second-order equation based on the sorption equilibrium capacity. The equation is of the form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2.3)$$

Integrating equation (2.3) with the boundary conditions earlier stated gives:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2.4)$$

where k_2 is the pseudo-second-order rate constant ($\text{mgg}^{-1}\text{min}^{-1}$) and together with the q_e is obtainable by a linear regression analysis of the $t / q_t = f(t)$ function. Ho and McKay [114] introduced two new parameters viz: initial adsorption rate $h_0 = k_2 q_e^2$ which defines the rate of adsorption as time tends to zero; and adsorption half life $t_{1/2} = 1/k_2 q_e$ which defines the time required for adsorption to reach half of the equilibrium capacity. Thus, equation 2.4 can also be written as:

$$qt = \frac{t}{\frac{1}{h_0} + \frac{1}{q_e}} \quad (2.5)$$

2.8.1.3. The Elovich Model

This model is based on adsorption capacity as established by the work of Zeldowitsch [92]. It is of the form:

$$\frac{dq_t}{dt} = a \exp(-bq_t) \quad (2.6)$$

where q_t is the sorption capacity at time t (mgg^{-1}), a and b are the Elovich parameters referring to the initial sorption rate ($\text{mgg}^{-1}\text{min}^{-1}$) and the desorption constant (mgg^{-1}) during any one experiment, respectively.

On integrating equation 3-6, applying the earlier stated boundary conditions, Chien and Clayton [26] further simplified the Elovich equation by assuming $a, b, t \geq 1$, thus arriving at:

$$q_t = \left(\frac{1}{b}\right) \ln(ab) + \left(\frac{1}{b}\right) \ln(t) \quad (2.7)$$

a and b are gotten by the linear regression analysis of the function $q_t = f(t)$.



2.8.2. Mechanistic Models

From a molecular standpoint, the adsorption of PAH molecules (and indeed any adsorbate) from an aqueous phase system onto an activated carbon has generally been described to proceed in three successive steps in the literature [131]:

- Transport of molecules from the bulk of the solution to the exterior surface of porous carbon particles through a boundary layer (liquid film or external diffusion);
- Diffusion of the PAHs through the interior pores of the carbon (intra particle or internal diffusion); and
- Adsorption of PAHs molecules onto the active sites on the interior surface.

These steps are schematically represented in Figure 3.

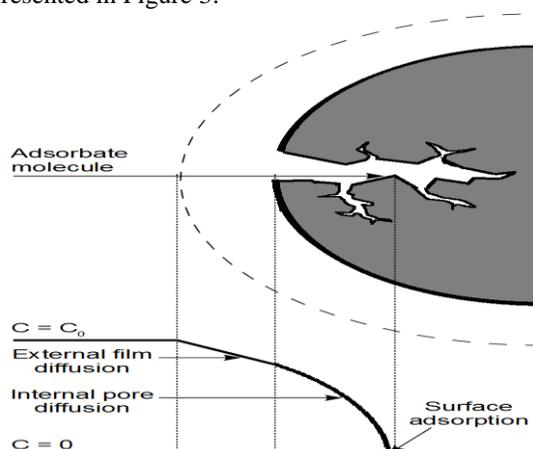


Figure 3: Schematic Diagram of Heterogeneous Adsorption Process

All three steps could potentially affect adsorption kinetics, while the third step also controls the specific adsorption capacity and intensity. Generally, one of the 3 steps offers the greatest resistance and is thus referred to as the rate limiting step of the whole sorption process. In practice however, unless chemical modifications occur during the sorption, the third stage is assumed to be too fast to contribute significantly to the overall sorption rate [79]. It is thus generally understood that slow sorption kinetics are caused by rate-limiting diffusive mass transfer [18,83].

2.8.2.1 Film Diffusion Model

The conditions under which the film diffusion controls the rate of adsorption as highlighted in the work of Mohan and his colleagues are under-listed as [52]:

- Low adsorbate concentration;
- Poor mixing condition;
- Small adsorbent particle size; and
- Very high affinity of adsorbate for adsorbent surface.

It is worthy of note that even in the absence of these conditions, the film diffusion still controls the initial stage of any adsorption process, since the last two steps take some time to set in. The equation proposed to govern a film diffusion controlled adsorption process is given by:

$$\ln \frac{C_e}{C_0} - k_s \frac{S_s}{V} t \quad (2.8)$$

where: k_s is the diffusion coefficient in m/s; S_s is the external adsorbent surface area in m^2 ; t is time in seconds; and V is the solution volume in m^3

2.8.2.2 Intra-particle Diffusion Models

A number of models have been used to describe the intra-particle diffusion of adsorbates into the porous structure of activated carbons. Valderrama et al [79] fitted their PAHs adsorption experiment data to the homogenous particle

diffusion model (HPDM) kinetic model based on solute extraction as discussed by [131] while another classical model employed by many researchers is the Weber-Morris intra-particle model [82].

$$q_t = k_i \sqrt{t} + C \quad (2.9)$$

where: q_t is amount adsorbed, mg/g; k_i = intra-particle diffusion rate constant, $\text{mgg}^{-1}\text{min}^{-1/2}$ t = time, s; C = constant related to resistance offered by boundary layer. The simplicity of this model has made it widely used in the literature [38,40,78].

2.9. Adsorption Isotherm

When an adsorbent is in contact with a surrounding fluid of a certain composition, adsorption takes place and after a sufficiently long contact time, equilibrium is reached between the sorbent and the surrounding fluid environment. At equilibrium, there is a defined distribution of solute between the fluid and solid sorbent phases. The adsorption isotherm is a functional expression relating the amount of solute adsorbed (q_e) on the sorbent to the equilibrium concentration (C_e) of solute in the fluid at a given temperature. To allow for comparison of different sorbent materials, the quantity adsorbed is always normalized by the mass of the sorbent used [131]. In the environmental application of sorbents, the predominant scientific basis for sorbent selection has been said to be the equilibrium isotherm, while the diffusion rate is generally secondary in importance [87]. This is rightly so since often times the diffusion rate is extremely fast, and as such a primary concern would be the capacity of the sorbent for the target compound within the operating temperature, concentration and pressure conditions as equilibrium is reached.

2.9.1. Classification of Adsorption Isotherms

In considering gas-solid systems, according to IUPAC [41], adsorption isotherms are categorized into six types and this helps better understand the nature of the adsorption process: monolayer, multilayer adsorption, capillary condensation or micropore filling. The categories are as given in the Figure 4 below:

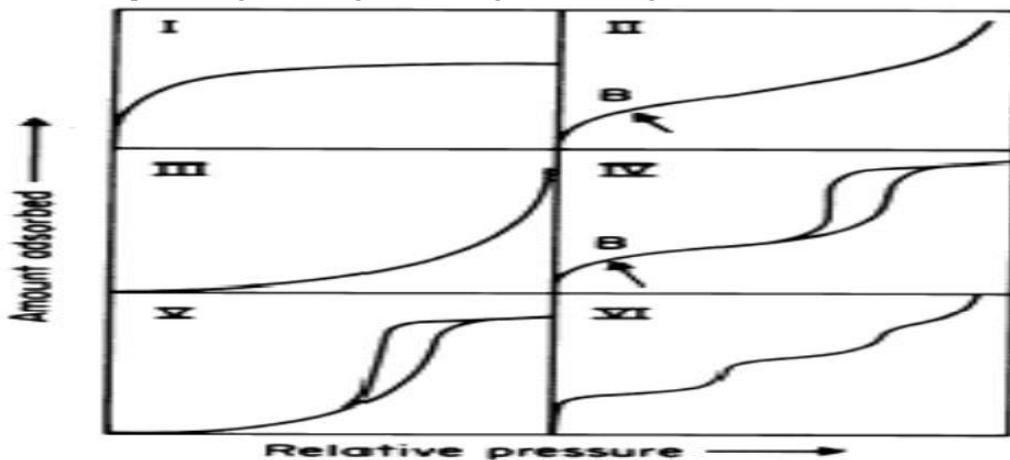


Figure 4: IUPAC Types of Adsorption Isotherm [41]

The Type I isotherms are given by microporous solids in which the pore size is not very much greater than the molecular diameter of the sorbate molecule. As such, the limiting uptake is governed by the accessible micropore volume with the saturation limit corresponding to the complete filling of the micropores. The Type II isotherm is obtained with a non-porous or macroporous adsorbent representing unrestricted monolayer-multilayer adsorption. Point B, the beginning of the almost linear middle section of the isotherm, is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption about to begin. Type III isotherm is convex to the p/p° axis over its entire range and therefore does not exhibit a Point B. They are uncommon and the adsorbate-adsorbate interactions play an important role in this kind of system. The characteristic feature of the Type IV isotherm is the hysteresis loop associated with capillary condensation taking place in mesopores. The initial part of the isotherm is attributed to monolayer-multilayer adsorption since it follows the same path as the corresponding part of a Type II isotherm. Type IV isotherms are given by many mesoporous industrial adsorbents. The Type V



isotherm is uncommon and is related to the Type III isotherm in that the adsorbent-adsorbate interaction is weak, but is obtained with certain porous adsorbents. The Type VI isotherm exhibits a stepwise multilayer adsorption on a uniform non-porous surface, in which the sharpness of the steps depends on the system and the temperature. The step-height represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly constant for two or three adsorbed layers.

2.9.2. Isotherm Models

Adsorption isotherms are described in many mathematical forms often based on empirical fittings while simplifying the physical properties and processes involved in the adsorption. The three major models that have mostly been used in fitting equilibrium adsorption isotherm of BTEX in the literature are highlighted below:

2.9.2.1. Langmuir Isotherm Model

This is about the simplest and most commonly used model. It is a semi-empirical isotherm derived from a proposed kinetic mechanism [45]. It is based on four assumptions all summed up in the sorbent being regarded as homogeneous:

1. Localized adsorption: molecules are adsorbed at a fixed number of well-defined localized sites.
2. No interactions between adsorbed molecules.
3. Monolayer adsorption: each site can only hold one adsorbate molecule
4. All sites are energetically equivalent.

The model has the linear form:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (2.10)$$

where C_e (mg/L) and q_e (mg/g) are the concentration of adsorbate and the adsorption capacity of the adsorbent at the equilibrium time, respectively. b (L/mg) is the Langmuir constant and Q_m (mg/g) is maximum adsorbent capacity. Q_m and b are attained by the slope and intercept of C_e/q_e versus C_e , respectively.

2.9.2.2. Freundlich Isotherm Model

Contrary to the monolayer and localized adsorption assumptions of Langmuir model, Freundlich [35] derived an empirical model with an exponential distribution of site energies and immobile adsorption. It suggests there exist multiple sets of sites on the surface of the adsorbent which is heterogeneous [13]. The model is of the form:

$$q_e = k_f C_e^{(1/n)} \quad (2.11)$$

where q_e is the equilibrium sorbed concentration (in mg of adsorbate/g of sorbent), and C_e (in mg/L) is the equilibrium solution phase concentration. K_f is the Freundlich constant related to the adsorption capacity, and $1/n$ is the intensity of adsorption. The Freundlich equation however does not give a limit of adsorption capacity (due to the $1/n$ th power of concentration), making the amount adsorbed go to infinity when concentration increases. This limits its application to concentrations below saturation where adsorption phenomena would no more be significant [73].

2.9.2.3. The Dubinin-Radushkevich Isotherm Model (D-R Model)

The D-R model is often employed to give insight into the adsorption mechanism by obtaining the apparent free energy of adsorption. The model is given by [32]:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (2.12)$$

where, q_m (mg/g) is the theoretical sorption capacity based on the isotherm, β (kJ/mol) is related to mean adsorption energy and ε (Polanyi Potential) is equal to $RT \ln(1 + 1/C_e)$. R (kJ/mol·K) is the universal gas constant and T (K) is temperature [131].

2.10 Adsorption thermodynamics



The feasibility of adsorption processes is evaluated by studying the thermodynamics parameters. Energetic changes during adsorption in terms of considering amount of heat being absorbed or released, dispersal of energy and amount of energy provided by the chemical reaction are quantified by standard enthalpy (H°), standard entropy (S°) and Gibbs free energy (G°) respectively. These parameters are essential for indicating the spontaneity of adsorption mechanism and defining the exothermic and endothermic adsorption processes. In adsorption experiments the thermodynamics parameters are determined using the Van't Hoff equation. The equation is applied after examining different temperatures effect on the adsorption by calculating the K_{eq} for each experimental run. Consequently, a plot of $\ln K_{eq}$ vs. $1/T$ can be obtained to estimate the values of ΔH^0 and ΔS^0 .

$$\ln K_{eq} = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (2.13)$$

Also, the Gibbs free energy isotherm equation is used depending on equilibrium constant values:

$$G = -RT \ln K_{eq}$$

where K_{eq} is the equilibrium constant and $K_{eq} = q_e/C_e$, C_e : is the equilibrium concentration (mg/L), q_e is the adsorption capacity at equilibrium (mg/L), R is universal gas constant, T is temperature, H and S are the standard enthalpy and entropy respectively.

Thermodynamics of phenol adsorption onto hexamethylene bispyridinium dibromide modified montmorillonite showed that the adsorption process is spontaneous, exothermic and with increased randomness [50]. The adsorption of phenol onto the specified clay has $G = 18$ kJ/mol and $H = 14.47$ kJ/mol [50]. The general Gibbs free energy range is (0 to -20 kJ/mol) for physical adsorption and for chemical adsorption is (-80 to -400 kJ/mol). Whereas, the enthalpy ranges for both physical and chemical adsorption is (2.1–20.9) kJ/mol and (80–200) kJ/mol respectively. Generally, the characterizations of adsorption process with respect to temperature change are explained on thermodynamics basis. Altering the temperature would have various impacts on the energetic changes based on the pollutant and adsorbent type and other conditions in the surrounding.

2.11. Characterization

Different types of clays are characterized before and after adsorption processes to reflect their distinctive properties and how the adsorption of solids organics takes place at clays surface [10]. The varied behavior of clays in adsorbing the organics estimated by the adsorption capacity is a consequence of the variation in pore size, specific area, infrared spectrum, morphology, structural geometry and texture. Among the adsorption studies analyzed for two decades, the most commonly applied techniques to demonstrate clays characterization include: X-Ray Diffraction Analysis (XRD), Fourier Transform Infrared (FTIR), Thermogravimetric analysis (TG), Scanning Electron Microscope (SEM), Zeta potential and Brunauer, Emmett, and Teller (BET) multipoint technique [10]. The above-mentioned techniques are widely used for various adsorption applications as each one of them depicts some features of the clays. The XRD is described by being one of the most helpful techniques to determine the structural geometry and the Basal spacing of clays [89]. FTIR assist to probe the molecular orientation of the intercalated surfactants within the organoclays by producing an infrared spectrum of functional groups stretching vibrations [89]. However, SEM gives images that show the morphology of clays surface whether it is regular, irregular or with fluffy appearance and how it is changed after adsorption or adding surfactants [89]. Also, Zeta potential analyzer conducts analysis through measuring the zeta potential of the clays which describe the electro kinetic in colloidal dispersion [28].

3. Conclusion

Utilization of natural and modified clays as sorbents has been frequently applied in environmental clean-ups to enhance pollution control at oil spill sites, control ground waters/wastewaters pollution. It has also aided in mitigating hazardous waste from the environment. Whilst clays have been considered abundantly available and cheap alternative adsorbents, the technical viability of clay sorption process depends on the efficiency of removing the organic contaminants presented in aqueous sources. A specific type of natural or organoclay could be suitable for one application but not for the others. Therefore, the main objective of this review is to highlights the adsorption capacity of different clays and modified clays toward various VOCs pollutants.



Acknowledgement

The Authors acknowledge the efforts and contributions of all Academic Staff of the Department of Pure and Industrial Chemistry, Abia State University, Uturu, Nigeria.

References

- [1]. Alberici R.M, Zampronio C.G., Poppi R.J., and Eberlin M.N (2002). Water solubilization of ethanol and BTEX from gasoline: on-line monitoring by membrane introduction mass spectrometry. *Analyst* 127 (2), 230–234.
- [2]. Castillo M., Oubina A and Barcelo D (1998) Evaluation of ELISA kits followed by liquid chromatography-atmospheric pressure chemical ionization-mass spectrometry for the determination of organic pollutants in industrial effluents. *Environ. Sci. Technol.* 32 (14), 2180–2184.
- [3]. Mazzeo D.E.C, Levy C.E, De Angelis D.D.F and Marinmorales M.A (2010) BTEX biodegradation by bacteria from effluents of petroleum refinery. *Sci. Total Environ.* 408 (20) 4334–4340.
- [4]. Costa A.S, Romão L.P.C, Araujo B.R, Lucas S.C.O, Maciel S.T.A, Wisniewski A and Alexandre M.D.R (2012) Environmental strategies to remove volatile aromatic fractions (BTEX) from petroleum industry wastewater using biomass. *Bioresour. Technol.* 105, 31–39.
- [5]. US EPA (United States Environmental Protection Agency), 2008. MARPOL 73/78. <<http://www.epa.gov/owow/OCPCD/marpol.html>>.
- [6]. Egwaikhide, P.A., Akporhonor, E.E and Okieimen, F.E. (2007). Utilization of Coconut Fibre Carbon in the removal of soluble petroleum fraction polluted water. *International Journal of Physical Sciences*, 2(2): 047-049
- [7]. Zhang L., Luo L., Zhang S. (2011). Adsorption of phenanthrene and 1,3-dinitrobenzene on cation-modified clay minerals, *Colloids Surf. A Physicochem. Eng. Asp.* 377: 278–283.
- [8]. Mitra S and Roy P (2011) BTEX: A serious ground-water contaminant. *Res. J. Environ. Sci.* 5 (5), 394–398.
- [9]. Bojes H.K. and Pope P.G. (2007) Characterization of EPA’s 16 priority pollutant polycyclic aromatic hydrocarbons (PAHs) in tank bottom solids and associated contaminated soils at oil exploration and production sites in Texas. *Regul. Toxicol. Pharmacol.* 47 (3), 288–295.
- [10]. Abdelrahman M.A., Shifa M.R.S, Rem. J., Mona H.G, Mustafa S.N., Abdelbaki B. and Samer A.(2019) Adsorption of organic pollutants by natural and modified clays: A comprehensive review. *J. Sep and Pur Technol.* 228: 1383-5866.
- [11]. Adachi A., Ikeda C., Takagi S., Fukao N., Yoshie E., Okano T, (2001). Efficiency of rice bran for removal of organochlorine compounds and benzene from industrial wastewater, *J. Agric. Food Chem.* 49:1309–1314.
- [12]. Ahmad M.A and Alrozi R. (2010). Optimization of Preparation Conditions For Mangosteen Peel-Based Activated Carbons For The Removal Of Remazol Brilliant Blue R Using Response Surface Methodology. *Chemical Engineering Journal* 165:883-890
- [13]. Ahn, S., Werner, D., Karapanagioti, H. K., Mcglothlin, D. R., Zare, R. N., & Luthy, R. G. (2005). “Phenanthrene and Pyrene Sorption and Intraparticle Diffusion in Polyoxymethylene, Coke, and Activated Carbon.” *Environ. Sci. Technol.*, 39: 6516 – 6526
- [14]. Aivalioti M., Vamvasakis L., and Gidaracos E. (2010). “BTEX and MTBE adsorption onto raw and thermally modified diatomite,” *Journal of Hazardous Materials*, 178, (1–3), 136–143.
- [15]. Aivalioti M., Pothoulaki D., Papoulias P., and Gidaracos E. (2012). “Removal of BTEX, MTBE and TAME from aqueous solutions by adsorption onto raw and thermally treated lignite,” *Journal of Hazardous Materials*, 207-208, 136–146.
- [16]. Akhtar M., Hasany S.N., Bhangar M.I, and Iqbal S, (2007). Sorption potential of Moringa oleifera pods for the removal of organic pollutants from aqueous solutions, *J. Hazard. Mater.* 141: 546–556.



- [17]. Anirudhan T.S., and Ramachandran M. (2006). Adsorptive removal of tannin from aqueous solutions by cationic surfactant-modified bentonite clay, *J. Colloid Interface Sci.* 299: 116–124.
- [18]. Ball, W. P., & Roberts, P. V. (1991). Long-term sorption of halogenated organic chemicals by aquifer material. *Environmental Science & Technology*, 25, 1223-1249.
- [19]. Bekins B.A., Cozarelli I.M., Godsy E.M., Warren E., Essaid H.I., and Tuccillo M.E. (2001). Progression of natural attenuation processes at a crude oil spill site: II. Controls on spatial distribution of microbial populations. *J. Contam. Hydrol.* 53 (3), 387–406.
- [20]. Barreca S., Orecchio S., and Pace A. (2014). The effect of montmorillonite clay in alginate gel beads for polychlorinated biphenyl adsorption: Isothermal and kinetic studies, *Appl. Clay Sci.* 99: 220–228.
- [21]. Boyd S.A, Shaobai S., Lee J.F. and Mortland M. (1988). Pentachlorophenol sorption by organoclays. *Clays Clay Miner.* 36, 125 – 130.
- [22]. Brigatti M., Corrodini F., Franchini G., Mazzoni S., Medici M. and Poppi L. (1995). Interaction between montmorillonite and pollutants from industrial wastewater: exchange of Zn^{2+} and Pb^{2+} from aqueous solution. *Appl. Clay Sci.* 9, 383 - 395.
- [23]. Carvalho M.N., Da Motta M., Benachour M., Sales D.C.S. and Abreu C.A.M. (2012). Evaluation of BTEX and phenol removal from aqueous solution by multi – solute adsorption onto smectite organoclay. *J. Hazard. Mater.* 239-240, 95 – 101.
- [24]. Chang, C., Chang, C., Holl, W., Ulmer, M., Chen, Y., & Gros, H. (2004b). “Adsorption Kinetics of Polyethylene Glycol from Aqueous Solution onto Activated Carbon” *Water Research*, 38(10), pp. 2559-2570.
- [25]. Chapelle F.H. (1999). Bioremediation of petroleum hydrocarbons contaminated ground water: the perspectives of history and hydrology. *Groundwater* 37 (1), 122–132.
- [26]. Chien S.H. and Clayton W.R. (1980) “Application of Elovich Equation to the Kinetics of Phosphate Release and Sorption in Soils” *Soil Sci. Soc. Am. J.* 44, pp. 265–268
- [27]. Chiriac R., Carre J., Perrodin, Fine L., and Letoffe J.M. (2007). Characterisation of VOCs emitted by open cells receiving municipal solid waste. *J. Hazardous Mater.* 149 (2), 249–263.
- [28]. Choi A.E.S., Roces S., Dugos N., Arcega A., Wan M.W., (2017). Adsorptive removal of dibenzothiophene sulfone from fuel oil using clay material adsorbents, *J. Clean. Prod.* 16: 267–276, <https://doi.org/10.1016/j.jclepro.2017.05.072>.
- [29]. Cruz-Guzman M., Celis R., Hermosin M.C., and Cornejo J. (2004). Adsorption of the herbicide simazine by montmorillonite modified with natural organic cations, *Environ. Sci. Technol.* 38: 180–186.
- [30]. de Paiva L.B., Morales A.R., and Valenzuela Diaz F.R. (2008). Organoclays: properties, preparation and applications. *Appl. Clay Sci.* 42(1-2), 8 - 24.
- [31]. dos Santos .A., Viante M.F., Pochapski D.J., Downs A.J., and Almeida C.A.P. (2018). Enhanced removal of p-nitrophenol from aqueous media by montmorillonite clay modified with a cationic surfactant, *J. Hazard. Mater.* 355: 136–144.
- [32]. Dubinin, M. M. (1960). “The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Non-Uniform Surfaces.” *Chem. Rev.*, 60: 235-241
- [33]. Egbuchunam T.O., Obi G., Okieimen F.E. and Tihminlioglu F. (2015). Effect of exchanged surfactant cation on the structure of kaolinitic clay. *J. Mater. Sci. Appl.* 2015, 1 – 14.
- [34]. El-Naas M.H., Acio J.A., and Et-Telib A.E. (2014). Aerobic biodegradation of BTEX: Progresses and prospects. *J. Environ. Chem. Eng.* 2, 1104–1122.
- [35]. Freundlich, H. (1926). “Colloid and Capillary Chemistry.” Matheun, London. 110 – 134.
- [36]. Grady S.J., and Casey G.D. (2001). Occurrence and distribution of methyl tert-butyl ether and other volatile organic compounds in drinking water in the Northeast and Mid-Atlantic regions of the United States. 1993-98, National water quality Assessment Program, National.
- [37]. Synthesis on Volatile Organic Compounds: Water Resources Investigation Report, 00-4228. United States Geological Survey, Denver.



- [38]. Graham, N., Chen, X.G., & Jayaseelan, S., (2001). "The Potential Application of Activated Carbon from Sewage Sludge to Organic Dyes Removal." *Water Science and Technology*, 43(2), 245-252.
- [39]. Gupta V.A., Sharma S., Yadav I.I., Mohan D, (1998). Utilization of bagasse fly ash generated in the sugar industry for the removal and recovery of phenol and P-nitrophenol from wastewater, *J. Chem. Technol. Biotechnol.* 170: 180–186.
- [40]. Ho, Y.S. & McKay, G., (1998). "Sorption of Dye from Aqueous Solution by Peat." *Chemical Engineering Journal*, 70(2), 115-124.
- [41]. International Union of Pure and Applied Chemistry, IUPAC (1985). "Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity." *Pure & Appl. Chem.*, 57 (4): 603—619
- [42]. Jaynes W.F., Vance G.F, (1999). Sorption of benzene, toluene, ethylbenzene, and xylene (BTEX) compounds by hectorite clays exchanged with aromatic organic cations, *Clays Clay Miner.* 47: 358–365.
- [43]. Kittrick, J.A. (1960). Cholesterol as a standard in the x-ray diffraction of clay minerals. *Soil Sci. Soc. Am. Proc.* 24:17-20
- [44]. Lagergren (1898), *Zur Theorie der Sogenannten Adsorption Geloster stoffe*, Kungliga Svenska Vetenskapsakademiens. Handlingar 24 (4), pp. 1–39.
- [45]. Langmuir, I.: (1916), 'The Adsorption of Gases on Plane Surface of Glass, Mica and Platinum', *J. Am. Chem. Soc.* 40, 1361–1368.
- [46]. Lin S.H., Hsiao R.C, Juang R.S. (2006). Removal of soluble organics from water by a hybrid process of clay adsorption and membrane filtration, *J. Hazard. Mater.* 135: 134–140.
- [47]. Lin S.H., and Huang C.Y, (1999). Adsorption of BTEX from aqueous solution by macroreticular resins, *J. Hazard. Mater.* 70: 21–37.
- [48]. Lin S.H., and Cheng M.J. (2002). Adsorption of phenol and m-chlorophenol on organobentonites and repeated thermal regeneration, *Waste Manag.* 22: 595–603.
- [49]. Lo B., Mak R., and Lee S. (1997). Modified clays for waste containment and pollutant attenuation. *J. Environ. Eng.* 123, 25 – 32.
- [50]. Luo Z., Gao M., Yang S., and Yang Q. (2015). Adsorption of phenols on reduced-charge montmorillonites modified by bispyridinium dibromides: Mechanism, kinetics and thermodynamics studies, *Colloids Surfaces A Physicochem. Eng. Asp.* 482: 222–230.
- [51]. Mirmohamadsadeghi S., Kaghazchi T., Soleimani M., Asasian N. (2012). An efficient method for clay modification and its application for phenol removal from wastewater, *Appl. Clay Sci.* 59, 8–12.
- [52]. Mohan, D., Gupta, V.K., Srivastava, S.K., & Chander, S., 2001. "Kinetics of Mercury Adsorption from Wastewater Using Activated Carbon Derived from Fertilizer Waste." *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 177(2-3), 169 – 181.
- [53]. Nourmoradi H., Nikaeen M. and Khiadani M. (2012). Removal of benzene, toluene, ethylbenzene and xylene (BTEX) from aqueous solutions by montmorillonite modified with non-ionic surfactant: Equilibrium, kinetic and thermodynamic study. *Chem. Eng. J.* 191, 341 – 348.
- [54]. Nourmoradi H., Nikaeen M. and Khiadani M. (2012). Multi-Component Adsorption of Benzene, Toluene, Ethylbenzene, and xylene from Aqueous solutions by Montmorillonite Modified with Tetradecyl Trimethyl Ammonium Bromide. *journal of chemistry*, 2013: 1-10.
- [55]. Obi Chidi, Okike U.N. and Okoye P. I. (2018). The Use of Organophilic Bentonite in the Removal Phenol from Aqueous Solution: Effect of Preparation Techniques. *Modern Chem Appl* 6: 258. doi:10.4172/2329-6798.1000258
- [56]. Oha T.U. (2017). Isotherm and Kinetic Studies of Some Selected Dyes Adsorption from Aqueous Solution Using Palm Fruit Fibre. M.Sc Thesis. Department of Pure And Industrial Chemistry. Abia State University, Nigeria.



- [57]. Olguí M.T. (2012). Adsorption of phenol onto surfactants modified bentonite, *J. Incl. Phenom. Macrocycl. Chem.* 1: 67–75.
- [58]. Olu-Owolabi B.I., Alabi A.H., Diagboya P.N., Unuabonah E.I., During R.A., (2017). Adsorptive removal of 2,4,6-trichlorophenol in aqueous solution using calcined kaolinite-biomass composites, *J. Environ. Manage.* 192: 94–99,
- [59]. Qu F., Zhu L. Yang K., Adsorption behaviors of volatile organic compounds (VOCs) on porous clays heterostructures (PCH), *J. Hazard. Mater.* 170: 7–12.
- [60]. Park S.J., Kim Y.B., Do Yeo S. (2008). Vapor adsorption of volatile organic compounds using organically modified clay, *Sep. Sci. Technol.* 43: 1174–1190
- [61]. Park Y., Sun Z., Ayoko G.A., Frost R.L. (2014). Removal of herbicides from aqueous solutions by modified forms of montmorillonite, *J. Colloid Interface Sci.* 415: 127–132.
- [62]. Park Y., Ayoko G.A., Horvath E., Kurdi R., Kristof J., Frost R.L. (2013). Structural characterization and environmental application of organoclays for the removal of phenolic compounds, *J. Colloid Interface Sci.* 393: 319–334.
- [63]. Reddy C.M., Arey J.S., Seewald J.S., Sylva S.P., Lemkau K.L., Nelson R.K., Carmichael C.A., McIntyre C.P., Fenwick J., Ventura G.T. and Van Mooy B.A. (2012). Composition and fate of gas and oil released to the water column during the Deepwater Horizon oil spill. *Proc. Natl Acad. Sci.* 109 (50), 20229–20234.
- [64]. Schmidt T.C., Haderlein S.B., Pfister R. and Forster R. (2004). Occurrence and fate modelling of MTBE and BTEX compounds in a Swiss Lake used as drinking water supply. *Water Res.* 38 (6), 1520–1529.
- [65]. Schouten N., van der Ham L.G.J., Euverink G.J.W., de Haan A.B. (2007). Selection and evaluation of adsorbents for the removal of anionic surfactants from laundry rinsing water, *Water Res.* 41: 4233–4241.
- [66]. Seifi L., Torabian A., Kazemian H., Bidhendi G., Azimi A., Farhadi F. and Nazmara S. (2011). Kinetic study of BTEX removal using granulated surfactant – modified natural zeolites nanoparticles. *Water, Air & Soil Pollut.* 219(1-4), 443 – 457.
- [67]. Sharmasarkar S., Jaynes W.F. and Vance G.F. (2000). BTEX sorption by montmorillonite Organoclays: TMPA, ADAM, HDTMA. *Water, Air & Soil Pollut.* 119, 257 – 273.
- [68]. Sharafimasooleh M., Bazgir S., Tamizifar M., and Nemati A. (2011). “Adsorption of hydrocarbons on modified nanoclays,” *IOP Conference Series Materials Science and Engineering*, 18, 182012.
- [69]. Shen Y.H. (2004). Phenol sorption by organoclays having different charge characteristics, *Colloids Surf. A Physicochem. Eng. Asp.* 232: 143–149.
- [70]. Shen Y.N. (2002). Removal of dissolved organic matter from water by adsorption-flocculation using organobentonite, *Environ. Technol.* 23: 553–560.
- [71]. Slack R.J., Gronow J.R. and Voulvoulis N. (2005). Household hazardous waste in municipal landfills: contaminants in leachate. *Sci. Total Environ.* 337, 119–137.
- [72]. Su F., Lu C., and Hu S. (2010). “Adsorption of benzene, toluene, ethylbenzene and p-xylene by NaOCl-oxidized carbon nanotubes,” *Colloid Surface A*, 353, 83–91.
- [73]. Suzuki, & Motoyuki (1990). “Adsorption Engineering.” Kodansha, Tokyo. 37-41.
- [74]. Telli-Karakoc F., Tolun L., Henkelman B., Klimm C., Okay O., & Schramm K.W. (2002). Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) Distributions in Bay of Marmara: Izmit Bay. *Environmental Pollution* 119: 383–397.
- [75]. Trivedi H.C., Patel V.M., and Patel R.D. (1973). “Adsorption of cellulose triacetate on calcium silicate,” *European Polymer Journal*, 9(6), 525–531.
- [76]. Tronczyński J., Munsch C., Heas-Moisan K., Guiot N., Truquet I., Olivier N., Men S. and Furaut A. (2004). Contamination of the Bay of Biscay by polycyclic aromatic hydrocarbons (PAHs) following the T/V “Erika” oil spill. *Aquat. Living Resour.* 17 (3), 243–259.
- [77]. Tunsaringkarn T., Siriwong W., Rungsiyothin A. and Nopparabundit S. (2012). Occupational exposure of gasoline station workers to BTEX compounds in Bangkok, Thailand. *Int. J. Occup. Environ. Med.* 3, 117–125.



- [78]. Valderrama, C., Cortina, J. L., Farran, A., Gamisans, X., & Lao, C. (2007). Kinetics of Sorption of polyaromatic Hydrocarbons onto Granular Activated Carbon and Macronet Hyper- Cross-Linked Polymers (MN200). *Journal of Colloid and Interface Science*, 310(1), 35-46.
- [79]. Valderrama, C., Gamisans, X., de las Heras, X., Farran, A., & Cortina, J. L. (2008). "Sorption Kinetics of Polycyclic Aromatic Hydrocarbons Removal Using Granular Activated Carbon: Intraparticle Diffusion Coefficients." *Journal of Hazardous Materials*, 157(2-3), 386-396.
- [80]. Vidal C.B, Raulino G.S.C., Barros A.L., Lima A.C.A., Ribeiro J.P., Pires M.J.R and Nascimento R.F (2012). BTEX removal from aqueous solutions by HDTMA – modified Y zeolite. *J. Environ. Manage.* 112, 178 – 185.
- [81]. Wang J., Gao M., Ding F., Shen T. (2018). Organo-vermiculites modified by heating and gemini pyridinium surfactants: Preparation, characterization and sulfamethoxazole adsorption, *Colloids Surfaces A Physicochem. Eng. Asp.* 546: 143–152.
- [82]. Weber Jr., W.J., & Morris, J.C., (1963). Kinetics of Adsorption on Carbon from Solution. *J. Sanit. Eng. Div. – ASCE* 89, 31–59.
- [83]. Wu .Y., Davis G.B, Barber C, Power T.R, Thierrin J, Patterson B.M, Rayner J.L and Qinglong W. (1999). The variability and intrinsic remediation of a BTEX plume in anaerobic sulphate-rich groundwater. *J. Contam. Hydrol.* 36 (3), 265–290.
- [84]. Xi Y., Zhou Q., Frost R. L. and He H. (2007). Thermal stability of octadecyltrimethylammonium bromide modified montmorillonite organoclay. *J. Colloid Inter. Sci.* 311, 347 – 353.
- [85]. Xiang Z., Lu Y., Gong X., and Luo G. (2010). Absorption and desorption of gaseous toluene by an absorbent microcapsules column, *J. Hazard. Mater.* 173: 243–248.
- [86]. Xin X.D., Wang J., Yu H.Q., Du B., Wei Q., Yan L.G. (2011). Removal of o-nitrobenzoic acid by adsorption on to a new organoclay: Montmorillonite modified with HDTMA microemulsion, *Environ. Technol.* 32:447–454,
- [87]. Yang, R.T. (2003). "Adsorbents: Fundamentals and Applications. Wiley and Sons, New Jersey. 17-19.
- [88]. Yang Q., Gao M., and Zang W. (2017). Comparative study of 2,4,6-trichlorophenol adsorption by montmorillonites functionalized with surfactants differing in the number of head group and alkyl chain, *Colloids Surfaces A Physicochem. Eng. Asp.* 520, 805–816.
- [89]. Yang Q., Gao M., Luo Z., and Yang S. (2016). Enhanced removal of bisphenol A from aqueous solution by organo-montmorillonites modified with novel Gemini pyridinium surfactants containing long alkyl chain, *Chem. Eng. J.* 285: 27–38,
- [90]. Yilmaz N., Yilmaz H., and Yapar S. (2007). Removal of Phenol Using TDTAB- and HDTAB Bentonites, *Energy Sources, Part A Recover. Util. Environ. Eff.* 29: 67–77.
- [91]. Yu J.Y., Shin M.Y., Noh J.H., and Seo J.J. (2004), Adsorption of phenol and chlorophenols on hexadecyltrimethylammonium-and tetramethylammonium-montmorillonite from aqueous solutions, *Geosci. J.* 8: 191–198.
- [92]. Zeldowitsch J. (1934). Uber den Mechanismus der Katalytischen oxydation von CO an MnOActa *Physicochim. URSS* 1, pp. 364
- [93]. Zeng Z., and Jiang J.Q. (2005). Effects of the type and structure of modified clays on adsorption performance, *Int. J. Environ. Stud.* 62:403–414.
- [94]. Zhu R., Chen Q., Zhou Q., Xi Y., Zhu J., and He H. (2016). Adsorbents based on montmorillonite for contaminant removal from water: A review, *Appl. Clay Sci.* 123: 239–258.
- [95]. Fayeminwo O.M., Daramola M.O., and Moothi, K. (2017). BETEX-compound in water -future trends and direction for water treatment. *Water SA* 43(4); 602-608.
- [96]. Cozzarelli I.M., Bekins B.A., Baedecker M.J., Aiken G.R., Eganjouse R.P. and Tuccillo M.E. (2001). Progression of natural attenuation processes at a crude-oil spill site: I. Geochemical evolution of the plume. *J. Contam. Hydrol.* 53 (3) 369–385.



- [97]. Camilli, R., Reddy, C.M., Yoerger, D.R., Van Mooy, B.O., Jakuba, M.V., Kinsey, J.C., McIntyre, C.P., Sylva, S.P. and Maloney J.V. (2010). Tracking Hydrocarbon Plume Transport and Biodegradation at Deepwater Horizon. *Science* 330 (6001) 201–204
- [98]. Pruden, A., Sedran, M., Suidan, M. and Venosa A. (2003). Biodegradation of MTBE and BTEX in an Aerobic Fluidized Bed Reactor. *Water Sci. Technol.* 47 (9) 123–128.
- [99]. Poulsen, M., Lemon, L. and Barker. J.F. (1992). Dissolution of Monoaromatic Hydrocarbons into Groundwater from Gasoline-Oxygenate Mixtures. *Environ. Sci. Technol.* 26 (12) 2483–2489.
- [100]. NHMRC (National Health and Medical Research Council, Australia) (2011). Australian Drinking Water Guidelines Paper 6 National Water Quality Management Strategy. National Health and Medical Research Council, National Resource Management Ministerial Council, Commonwealth of Australia, Canberra.
- [101]. Abumaizar R.J., Kocher W and Smith E.H. (1998). Biofiltration Of BTEX Contaminated Air Streams Using Compost-Activated Carbon Filter Media. *J. Hazardous Mater.* 60 (2) 111.
- [102]. Leusch F., and Bartkow M. (2010). A Short Primer on Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) In the Environment And In Hydraulic Fracturing Fluids. Smart Water Research Centre, Griffith University. Url: <https://www.ehp.qld.gov.au/management/coalseam-gas/pdf/btex-report.pdf>. (Accessed 10 October 2017).
- [103]. Neff, J.M. (2002). Bioaccumulation in Marine Organisms: Effect of Contaminants from Oil Well Produced Water (1st Edn). Elsevier Publishing, Amsterdam.
- [104]. Meniconi M.D.F., Gabardo I.T., Carneiro M.E.R., Barbanti S.M., Da Silva G.C., and Massonne C.G. (2002). Brazilian Oil Spills Chemical Characterization–Case Studies. *Environ. Forensics* 3 (3–4) 303–321.
- [105]. Lu, Q., Sorial, and G. A. (2004). Adsorption of Phenolics on Activated Carbon–Impact of Poresize and Molecular Oxygen. *Geochim. Cosmochim. Acta* 55, 671–679.
- [106]. Essaid H.I., Cozzarelli I.M., Eganhouse R.P., Herkelrath W.N., Bekins B.A., and Delin G.N. (2003). Inverse Modeling of BTEX Dissolution and Biodegradation at the Bemidji, Crude-Oil Spill Site. *J. Contam. Hydrol.* 67 (1) 269–299.
- [107]. Margesin R, Walder G. and Schinner F. (2003). Bioremediation Assessment of a Btex-Contaminated Soil. *Acta Biotechnol.* 23 (1) 29–36.
- [108]. Das N. and Chandran P. (2011). Microbial Degradation of Petroleum Hydrocarbon Contaminants: An Overview. *Biotechnol. Res. Int.* 2011 1–13.
- [109]. Ranck J.M., Bowman R.S., Weeber J.I, Katz L.E. and Sullivan E.J. (2005) BTEX Removal from Produced Water Using Surfactant modified Zeolite. *J. Environ. Eng.* 131 (3) 434–442.
- [110]. Dorea H.S., Bispo J.R., Aragão K.A., Cunha B.B., Navickiene S., Alves J.P., Romao L.P. and Garcia C.A. (2007). Analysis of BTEX, PAHs and Metals in the Oilfield Produced Water in the State of Sergipe, Brazil. *Microchem. J.* 85 (2) 234–238.
- [111]. Roco M.C. (2011). The Long View of Nanotechnology Development: The National Nanotechnology Initiative at 10 Years. *J. Nanoparticle Res.* 13 (2) 427–445.
- [112]. Chiriac R., Carre J., Perrodin Y., Fine L. and Letoffe J.M. (2007). Characterisation of Voc's Emitted By Open Cells Receiving Municipal Solid Waste. *J. Hazardous Mater.* 149 (2) 249–263.
- [113]. Robinson H.D., Knox K., Bone B.D. and Picken A. (2005). Leachate Quality From Landfilled MBT Waste. *Waste Manage.* 25 (4) 383–391.
- [114]. Mackay D.M., De Seyes N.R., Einarson M.D., Feris KP., Pappas A.A., Wood I.A., Jacobson L., Justice L.G., Noske M.N., Scow K.M. And Wilson J.T. (2006). Impact of Ethanol on the Natural attenuation of benzene, toluene, and o-xylene in a normally sulfate reducing aquifer. *Environ. Sci. Technol.* 40 (19) 6123–6130.
- [115]. Cadena A.M., Fortune S.M, Flynn J.L. Heterogeneity in tuberculosis. *Nature reviews Immunology.* 2017; 17(11): 691–702.
- [116]. El-Geundi M.S., Eman A.A., Reda M.A., Nabilia S. (2014). Determination of specific surface area of natural clay by comparative methods. *Int. J. Sci. Eng. Tech. Res.* 3(8): 2100-2104



- [117]. Yunfei X., (2006). Synthesis, Characterisation and Application of Organoclays PhD Thesis. School of Physical and Chemical Sciences, Queensland University of Technology, Australia.
- [118]. Anon. (1978). Bentonite, sepiolite, attapulgite, etc. — swelling markets for active clays. *Ind. Miner.*, March, 49–91.a
- [119]. Yariv, S., (2002). Introduction to organo-clay complexes and interactions. In: Yariv, S., Cross, H. (Eds.), *Organo-Clay Complexes and Interactions*, Marcel Dekker, New York, pp. 39–111.
- [120]. Boyd, S.A., Shaobai, S., Lee, J.F., Mortland, M.M., (1988c). Pentachlorophenol sorption by organoclays. *Clays Clay Miner.* 36, 125–130.
- [121]. Porter T.L., Eastman M.P., Zhang D.Y., Hagerman M.E. (1997). Surface Polymerization of Organic Monomers on Cu(II)-Exchanged Hectorite, *J.Phys.Chem.B.* 101(51): 11106-11111.
- [122]. Mortland, M.M., Saobai, S., Boyd, S.A., 1986. Clay-organic complexes as adsorbents for phenol and chlorophenols. *Clay Miner.* 34, 581–595.
- [123]. Barrer, R.M., Kelsey, K.E., (1961). Thermodynamics of interlamellar complexes. *Trans. Faraday Soc.* 57, 452–462.
- [124]. Lee, S.Y., Kim, S.J., (2002). Expansion of smectite by hexadecyltrimethylammonium. *Clays ClayMiner.* 50, 435–445.
- [125]. Beneke, K., Lagaly, G., The brittle mica-like KNiAsO₄ and its organic derivatives, *Clay Minerals*, 1982, 17: 175–183.
- [126]. Jaynes, W.F., Boyd, S.A., 1991a. Clay mineral type and organic-compound sorption by hexadecyltrimethylammonium-exchanged clays. *Soil Sci. Soc. Am. J.* 55, 43–48.
- [127]. Jouany C., Chassin P. (1987). Determination of the surface energy of clay—organic complexes by contact angle measurements, *J.colloid and surface.* 27(4): 289-303.
- [128]. Lagaly, G., 1995. Surface and interlayer reactions: bentonites as adsorbents. In: Churchman, G.J., Fitzpatrick, R.W., Eggleton, R.A. (Eds.), *Clays Controlling the Environment. Proceedings of the 10th International Clay Conference, Adelaide, Australia, 1993.* CSIRO Publishing, Melbourne, pp. 137–144.
- [129]. Margulies L., Rozen H. and Nir S, (1988) Model for Competitive Adsorption of Organic Cations on Clays, *Clays and Clay Minerals*, 36, 270-276.
- [130]. Rytwo, G., Tropp, D., Serban, C., (2002). Adsorption of diquat, paraquat and methyl green on sepiolite: experimental results and model calculations. *Appl. Clay Sci.* 20, 273–282.
- [131]. Ayodeji A. (2017). Understanding The Adsorption Of Polycyclic Aromatic Hydrocarbons From Aqueous Phase Onto Activated Carbon M.Sc. Thesis, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Canada.

