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REVIEW PAPER

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A review on adsorption of organic pollutants on clay surface

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Abstract

Adsorption method is commonly used to eliminate different pollutants, especially organic pollutants from water on adsorbents. Different types of adsorbents are used to adsorbed organic pollutants like zeolite, siliceous materials, chitosan, and activated carbon, but to limit the scope, our review focuses only on different types of clay adsorbents for the removal of organic pollutants. The clay is an efficient and low cost adsorbent that attracted the attentions of the researchers. On the other hand, organic pollutants are often detected in industrial wastewaters and mostly these are known to be highly toxic and carcinogenic in nature. This review, compiled different types of clay adsorbents and organic pollutants (dyes, pharmaceutical products, herbicides, fungicides, pesticides, oil spills, and other phenolic organic compounds). The review describes different clay adsorbents, their molecular structure and their characteristics as well as discusses the mechanisms that how organic pollutants adsorbed on the clay surface.

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Introduction

Pollution remediation and wastewater treatment for providing safe and clean water for drinking and other activities is the greatest challenge of the 21st century (Dixit *et al.* 2009).

The wastewaters contain various pollutants that are highly toxic even at low concentration and cause server diseases in plants, animals and humans (Cooney, 1998). Generally there are two major sources of water pollution, direct and indirect. Direct contamination sources comprise of effluent discharges from industries, refineries and wastes treatment. Indirect contamination sources include pollutants that enter the water reservoirs from ground water and atmosphere through rain. Contaminants on the other hand are of two broad categories such as organic and inorganic (Vijayaraghavan, 2008).

Inorganic water pollutants includes acidic industrial discharges, fertilizer and metals while organic water pollutants include. Organic pollutants include pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals, proteins and carbohydrates and different types of dyes etc (Asim *et al.* 2012, Barceló, 2005).

These compounds enter into the environment by sewage water, oil effluents, agricultural activities and industrial wastewater etc (Matthes, 2000).

The organic pollutants, for example the derivatives of benzene are highly toxic, even at low concentration and adversely affect plants, animals and humans life (Naseer *et al.* 2012). Due to their continuous and excessive use, these compounds enter into the environment by sewage water, oil effluents, agricultural activities and industrial wastewater etc (Klahre *et al.* 2004). Several systems have been employed for the removal of organic contaminant through water, like adsorption, coagulation, filtration, precipitation, electrodialysis and membrane separation (Guo *et al.* 2009).

All these conventional have their own merits and demerits. High regeneration costs, operational complexity, slow uptake of pollutants, longer equilibrium times, poor efficiencies at low concentrations etc. are the key limitations of these techniques. Adsorption on solid surfaces, on the other hand is the more efficient and low cost method for the removal of many organic compounds (Kooli, 2013).

In the past year researchers have more interested in recovering the inorganic adsorbents from water especially clay which is the more efficient adsorbent for the removal of organic pollutants (Rouquerol *et al.* 2013). Mostly these adsorbents are used which include activated carbon (Nouri, Haghseresht *et al.* 2002, Pereira, Soares *et al.* 2003), clay minerals (Celis, *et al.* 2000), zeolites (Oliveira, Petkowicz *et al.* 2004), metal oxides (Wu, 2004), agricultural wastes (Robinson *et al.* 2002) biomass (Loukidou, *et al.* 2003) and polymeric materials (Atia, *et al.* 2003).

Although the literature reports a wide range of adsorbents and pollutants, but to limit the scope, our review takes into account only the removal of organic pollutants on the surface of clay as an adsorbent.

The clay is an efficient adsorbent and the organic pollutants are frequently detected in industrial wastewaters and some of them are known to be very toxic and carcinogenic.

Different types of adsorbents

Commercial activated carbons

Among all the adsorbents commercial activated carbon (CAC) is an effective adsorbent used for the elimination of organic pollutants. (Derbyshire, Jagtoyen *et al.* 2001, Babel and Kurniawan 2003).

CAC is most effective adsorbent due to their structural characteristics, large surface area (500-2000m²/g) due to porous structure and easily modified to increase its adsorption properties. However activated carbon have certain disadvantages (Babel and Kurniawan 2003).

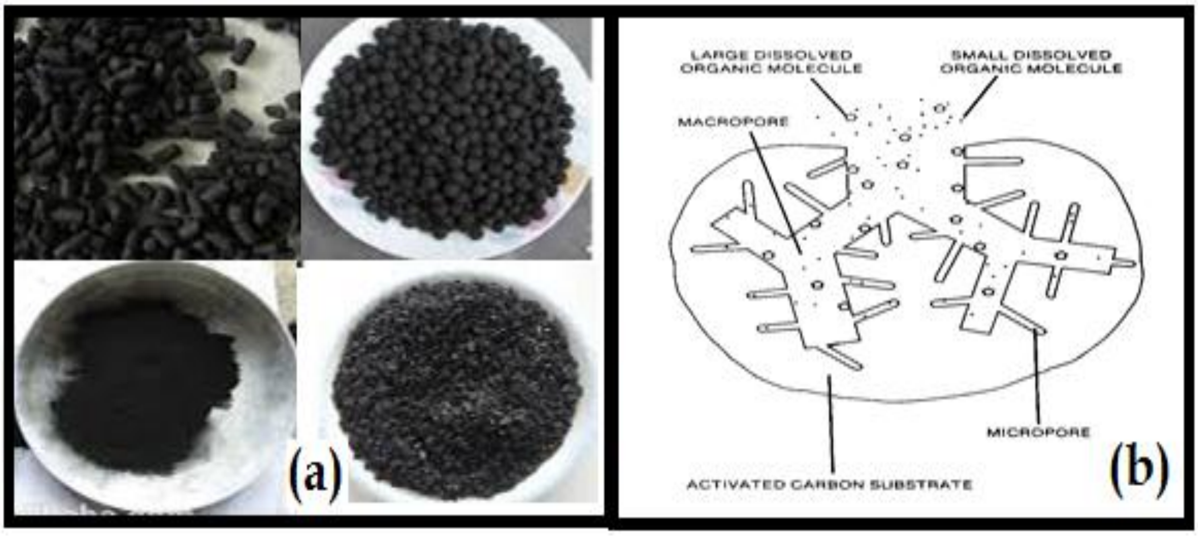

Fig. 1. (a) Physical appearance of activated carbon (b) Representation of activated carbon particles.

It is quite an expensive adsorbent. Several raw materials have been used in the production of activated carbon (Ali *et al.* 2012). Many agricultural and industrial wastes contain carbonaceous chars which is further activated to produce porous adsorbents. Two main forms of activated carbon can be used for water treatment: powder activated carbon and granular activated carbon.

Chitosan

It is a bio-sorbent and commercially extracted from crustaceans, crabs, krill, and Cray fish. Its chemical name is (1, 4)-2-amino-2-deoxy-β-D-glucan (Ba, *et al.* 2014). Chitosan contains 2-acetamido-2-deoxy-b-D-glucopyranose and 2-amino-2-deoxy-b-D-glucopyranose deposits (Crini 2006). Chitosan is low cost adsorbent as compared to activated carbon and it contain large amount of amino and hydroxyl functional groups that enhanced its adsorption capacity towards phenolic compounds, dyes and metal ions (Kumar 2000, Guibal 2004, Varma, Deshpande *et al.* 2004). Chitosan show some limitation that's why it needs some modification because chitosan weak hydrolytic strength as well as highly swell able in aqueous medium.

Zeolite

Zeolite is a naturally occurring highly porous aluminosilicate materials. Zeolites have high ion-exchange capacity, large surface area and low cost adsorbent (Crini and Morcellet 2002). Zeolite contain more than 40 naturally occurring species.

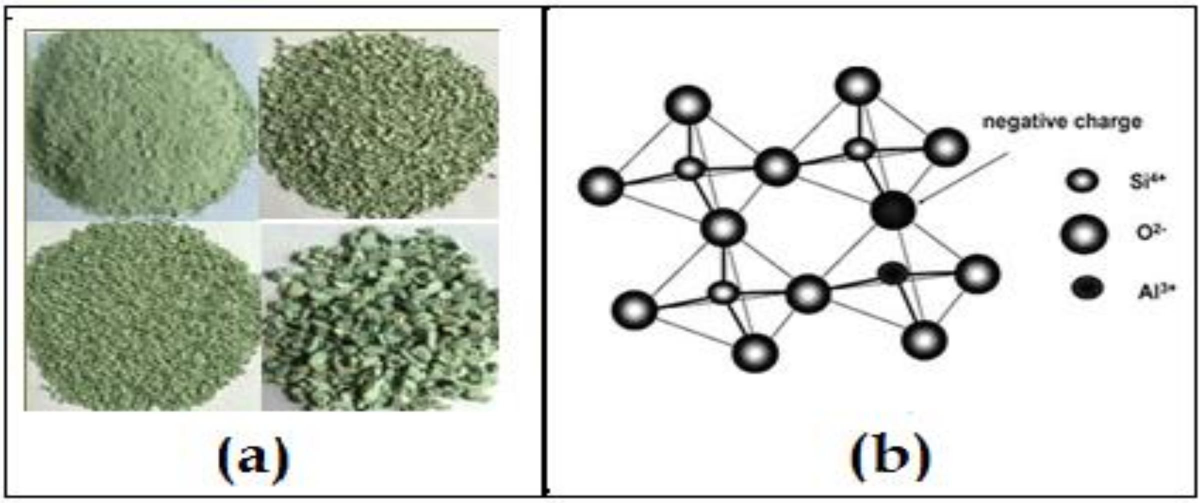

Fig. 2. (a) Physical appearance of Zeolite (b) Molecular structure of Zeolite.

However, the most abundant specie of zeolite is clinoptilolite, a mineral of the heulandite group. It is not a good sorbent in removing the organic pollutants. Zeolite formed by coal fly ash, modified with hexadecyltrimethylammonium (HDTMA) used for removing bisphenol A (BPA) from waste water. Recently, bio-zeolite was used in removing pyridine and quinolone (Ali, *et al.* 2012).

Siliceous materials

Natural siliceous adsorbents like silica beads, alunite, glasses, dolomite and perlite are easily available, abundance in nature and low cost adsorbents are strong candidates for waste water treatment (Crini and Morcellet 2002). Due to the presence of silanol groups on the surface of silica beads provided hydrophilic surface attracted particular attention (Harris, *et al.* 2001, Woolard, *et al.* 2002).

Siliceous materials that have porous structure, large surface area and mechanically stable sorbent used for removing pollutants from waste water (Crini and Morcellet 2002).

Siliceous materials are restricted toward of pH less than 8 because of their low resistance near to alkaline solutions (Ahmed and Ram 1992). Today silica-based materials have been recognized to adsorbed organic pollutants from wastewater (Cooper and Burch 1999, Parida, Dash *et al.* 2006, Mangrulkar, Kamble *et al.* 2008). To enhance the adsorption capacity of siliceous materials towards dye, so it needs some modification by silane coupling agents with the amino functional group (Krysztafkiewicz, Binkowski *et al.* 2002). Modified Silica beads have more potential for adsorbing acidic dye from wastewater (Phan, Bacquet *et al.* 2000).

Perlite is another type of siliceous material have silica content greater than 70% and are low cost and easily available adsorbent, obtained from glassy volcanic rocks (Crini and Morcellet 2002).

Fig. 3. Silica gel beads, siliceous material.

Clay

One of an effective and low cost adsorbents is calys and clay minerals. Clay minerals are swell on exposure to water because of its swelling tendency.

Different clays and clay minerals can be used as a best adsorbents. Naturally abundant clay have a unique properties high ion exchange capacity, large surface area, micro- and meso- porosity and swelling properties. To make a clay as a best adsorbent so its need some modification. Now a days modify clay-based adsorbent can be used for the removal of pollutants (Fogler and Srinivasan 1988, Boyd 1993).

Modification of clay surface depends on cation exchange capacity (CEC) of the clay which is defined as milli equivalents of the anionic sites per unit gram of the clay (Shichi and Takagi 2000).

The competences of the intercalations are dependent on the type of clays and intercalated molecules.

To modify the structure of clay by replacing the inter layer cations (Na,K,Ca) (Barrer 1989).

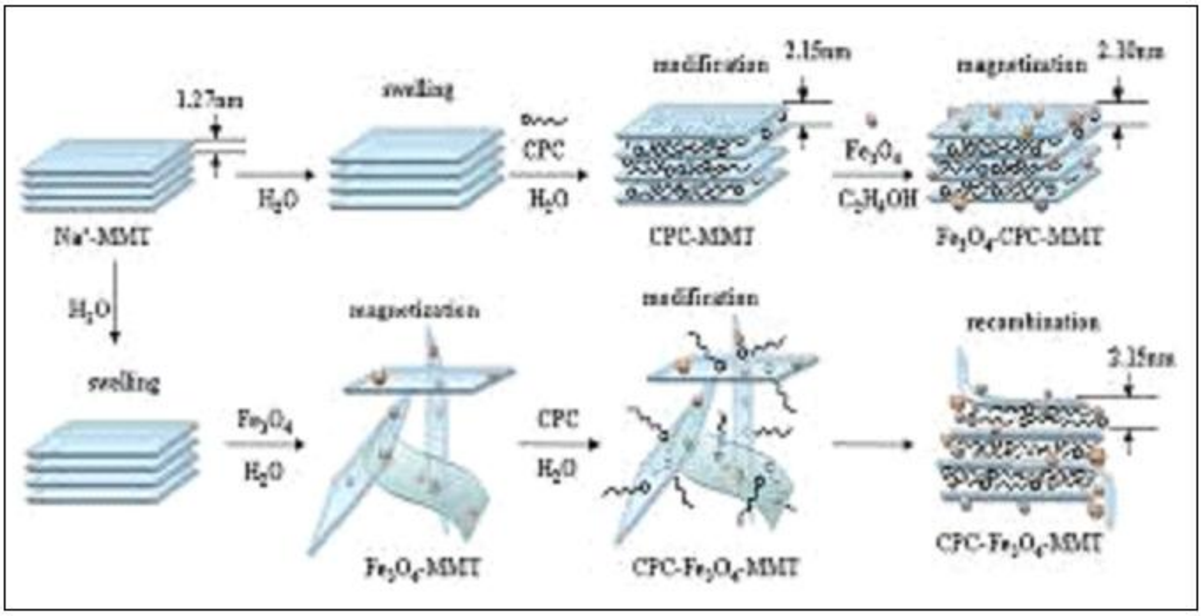

Fig. 4. Modification of Clay surface.

There are two main procedure to modifying the clay. The first one is reffered to as organo-clay exchange the natural interlayer cations with organocations such as tetramethylammonium (Lee, *et al.* 1990), dodecyl-trimethylammonium (Pal and Vanjara 2001), hexadecyl-trimethylammonium (Wibulswas, White *et al.* 1999). The second category includes metal oxide pillaredclays (PILCs) formed by exchanging the interlayer cations with highly charged polymeric metal species, while oxide pillared materials with a bi-dimensional porousnetwork can be obtained by subsequent calcination (Pinnavaia, Tzou *et al.* 1984) PILCs prepared with a number of different polyoxocations (e.g. Al, Ni,Zr, Fe, Cr, Mg, Si) and multimetallic species have been reported (Montarges, Michot *et al.* 1995, Frini, Crespin *et al.* 1997, Bergaoui, Mrad *et al.* 1999).

A various types of procedures have been used for modifying the clay minerals to enhance its adsorption capacity (An and Dultz 2007, Zhou 2011), including acid activation (Steudel, Batenburg *et al.* 2009), dealing with cationic surfactants (He, Frost *et al.* 2006), treatment with thermal activation (Toor and Jin 2012), intercalation of polymer(De Paiva, Morales *et al.* 2008), grafting with inorganic and organic anions, and intercalation of organic compounds (Liu and Zhang 2007).

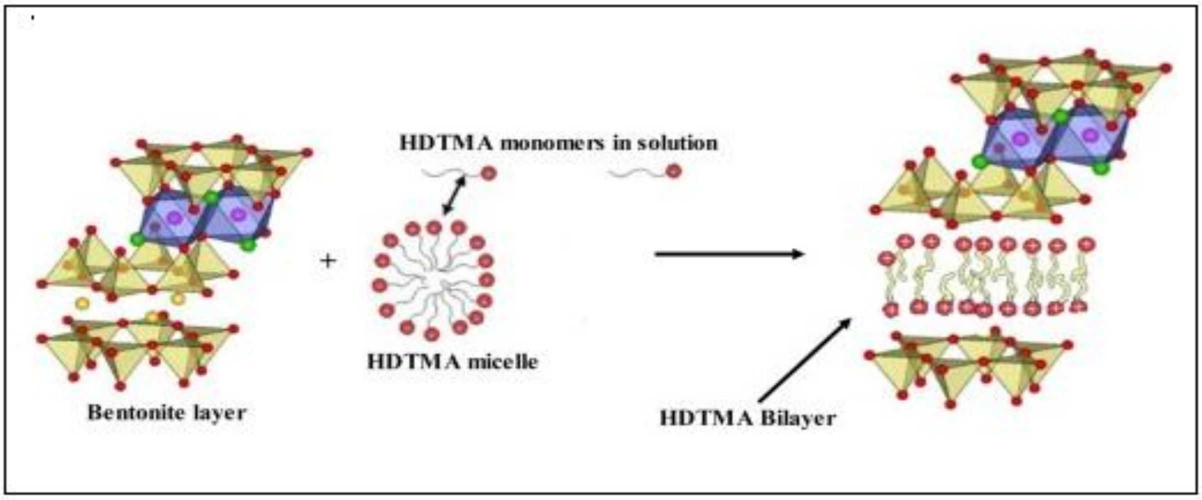

Fig. 5. Modification of clay through surfactant HDTMA.

Types of clay

There are four basic types of clay which are given below.

1. Kaolinite
2. Smectite
3. Illite
4. Chlorite

Kaolinite

It include dioctahedral minerals and trioctahedral minerals.

Dioctahedral: kaolinite, dickite, halloysite and nacrite.

Trioctahedral minerals: include antigorite, chamosite, chrysotile and cronstedite. Kaolinite have general formula of $Al_2Si_2O_5$ $(OH)_4$ (Moore and Reynolds 1989). Kaolinite have chemical composition of 39.8% alumina, 46.3% silica and 13.9% water (Murray 1991). Kaolinite exhibits white or nearly white in colour and hardness about 1.5 on the Mohs scale (a scale of hardness based on the ability of one mineral to scratch other and the hardness of minerals is mainly controlled by the strength of the bonding between the atoms and partly by the size of the atoms actually it is measure of the resistance of the mineral to scratching).

Fig. 6. Physical appearance of Kalonite.

Structure

Kaolinite contain silicate sheets (Si_2O_5) that are joined with aluminum oxide/hydroxide layers $(Al_2(OH)_4)$ called gibbsite layers (Moore and Reynolds 1989). One tetrahedral sheet that is a silicate mineral joined with octahedral sheet of alumina through oxygen atoms (Zussman, Howie *et al.* 1992). In dioctahedral minerals, the octahedral sheet is composed of aluminium, while in trioctahedral minerals, the tetrahedral sheet is composed by iron and magnesium (Adeyemo, Adeoye *et al.* 2017).

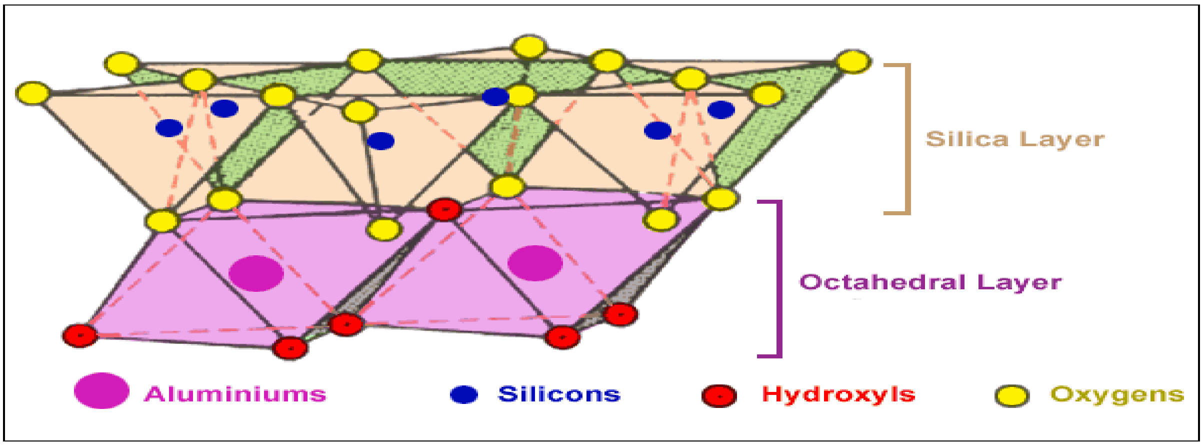

Fig. 7. Molecular structure of kaolinite clay.

Kaolinite is a non-swelling clay (Chen and Hayes 1999) and also the least reactive clay (Suraj, Iyer *et al.* 1998).

Fig. 8. Montmorillonite clay.

Smectite

Smectite is a non-metallic clay mineral with general formula $(Ca, Na, H)(Al, Mg, Fe, Zn)_2(Si, Al)_4O_{10}(OH)_2\text{-}nH_2O$ (Grim 1962). Smectite comprises white, tan, brown or brownish green or blue-green in color. Smectite is chemically composed on sodium, calcium, magnesium, iron, and lithium aluminum silicates. Smectite is mainly consist on a three-layered clay mineral as compared to kaolinite that is a double layer clay. Out of three layer, it contain two silica tetrahedral sheets and in the center joined with one octahedral sheet. Smectite have high cations exchange capacity that comprises 60-100 m Eq/100 grams of clay. Smectite contain particularly small sized particles which gives a clay to large surface area and a high structural charge (up to1000 meq kg^{-1}), imparting them a high degree of sorption capacity.

It contains following clay minerals: Montmorillonite, beidellite, vermiculite, bentonite, pyrophyllite, talc, sauconite, saponite, Hectorite and nontronite.

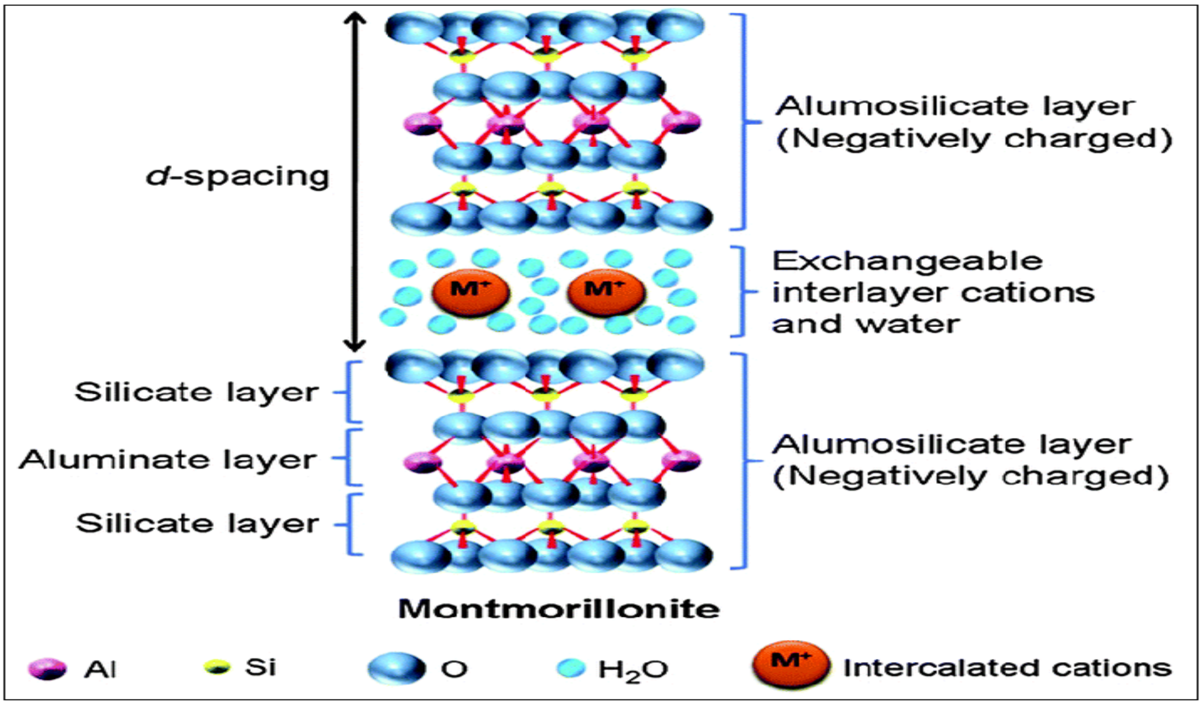

Fig. 9. Structure of Montmorillonite clay.

Montmorillonite and beidellite

Montmorillonite and Bedillite both clays are 2:1 dioctahedral smectite clay and have same cation exchange capacity. Montmorillonite are generally expressed as $M_x(Al_2\text{-}xMg_x)(Si_4)O_{10}(OH)_2{*}nH_2O$ and beidellite are $M_x(Al_2)(Si_4\text{-}xAl_x)O_{10}(OH)_2{*}nH_2O$. Montmorillonite clay is differ from beidellite on the basis of structure, the layer charge of montmorillonite clay is present in the hidden octahedral sheet but the layer charge is available in visible octahedral sheet (Brandt and Kydd 1997).

Montmorillonite is a phyllosilicate mineral that contain a microscopic crystals (Jaafar 2006).

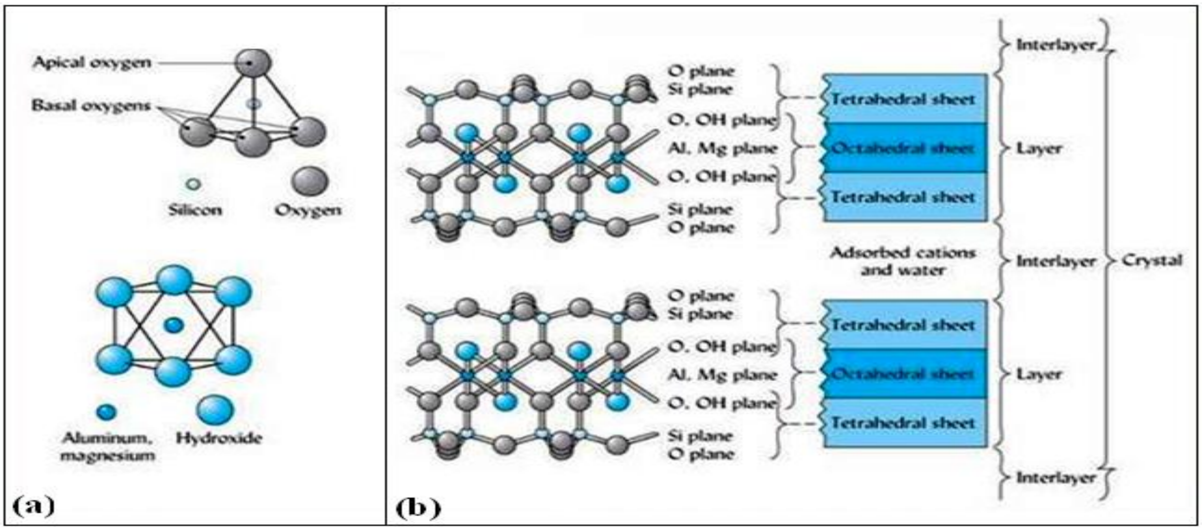

Fig. 10. Structure of Bentonite clay.

It is a low cost adsorbent and it price is US$ 0.04–0.12/kg), it is 20 times cheaper than activated carbon. The swelling capacity of montmorillonite clay is not so good in water as compared to hectorite (Tapia Estévez, López Arbeloa *et al.* 1993).

The poor swelling property of montmorillonite is due large particle size as well as strong interaction of clay layer with inter-lamellar species. Montmorillonite comprises Ca- montmorillonite and Na montmorillonite. In the interlayer space there is a one water layer in Sodium montmorillonites and two water layer in calcium montmorillonites Montmorillonite is a 2:1 type clay, two tetrahedral sheet of silica that enveloping one octahedral sheet of alumina (Shakir, Ghoneimy *et al.* 2008).

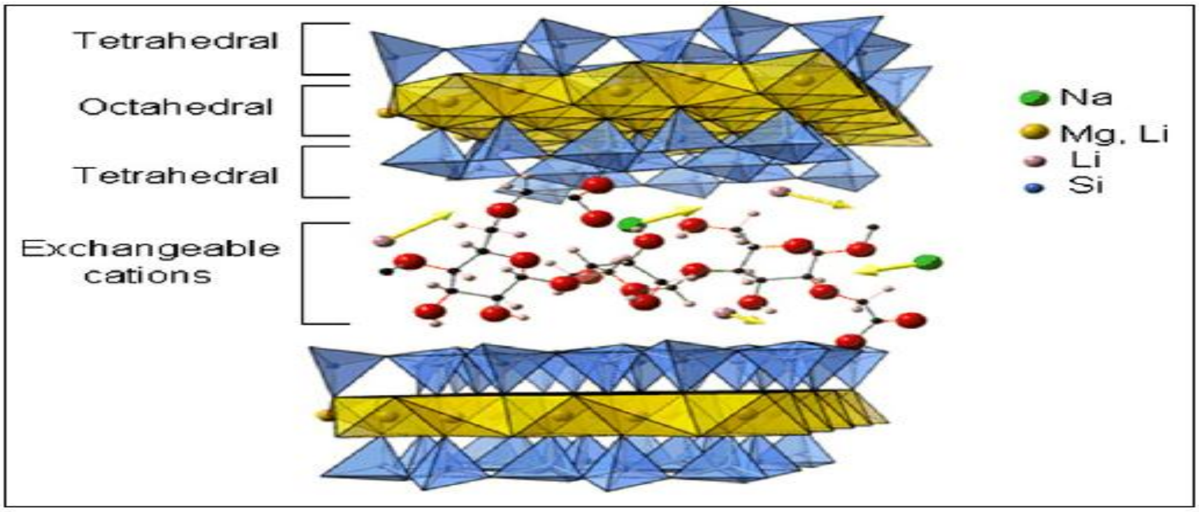

Fig. 11. Structure of Vermiculite.

In the tetrahedral sheets, Al^{3+}can substitute for $Si^{4+}$and in the octahedral sheets Mg^{2+} or Zn^{2+}can replace Al^{3+}.

These type of replacements in the clay lattice consequence into a net negative charge on the clay surface (Stumm 1981).

Bentonite

Bentonite is usually obtained from weathering of volcanic ash. Bentonite is a 2:1 layered silicate and expand on exposure to water.

The inner layer is octahedral sheet that is situated between two tetrahedral sheets.

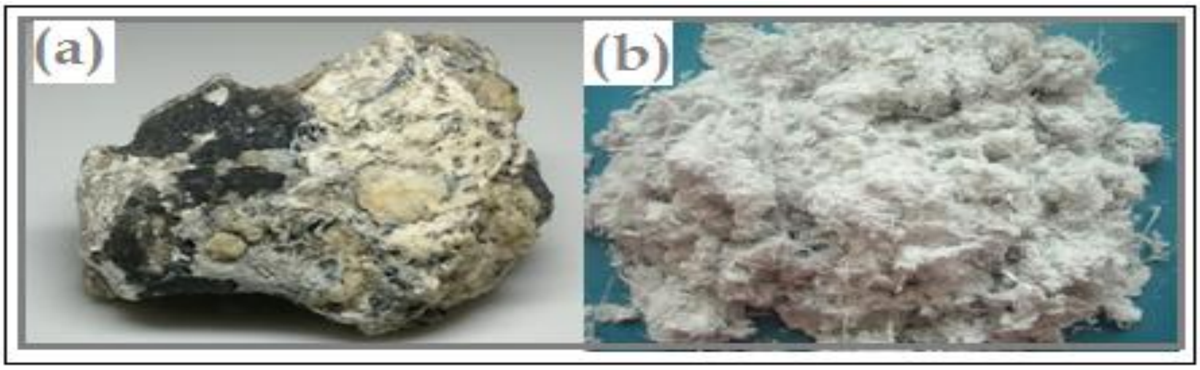

Fig. 12. Physical Appearance of (a) Palygorskite, (b) Sepiolite.

Structure of Bentonite clay

Commercially there are two main forms of bentonite were used sodium bentonite and calcium bentonite. Sodium bentonite swells up due to its excellent colloidal properties (Odom 1984).Sodium Bentonite expand on exposure to water. Bentonite have more adsorbing capacity towards different chemicals like amines (Breen 1991), organic pigments (bcarotenes) (Gonzalez-Pradas, Villafranca-Sanchez *et al.* 1991), cations (Ni, Zn), phenol and ketones (Stockmeyer and Kruse 1991), and non-ionic contaminants (Smith and Jaffé 1994).

Vermiculite

Vermiculite is a mica-type silicate have large surface area and strong adsorption capacity towards pollutants due to layered structure. Vermiculite is a hydrous magnecium aluminum silicate clay mineral, particularly contain magnecium in the interlayer space and slightly consist on Ca, K and Na (Silva, de Souza *et al.* 2012). Vermiculite is a clay mineral present in two form: in dioctahedral form expressed as M_x (Al_2^- yFe_4^{3+}) (Si_4–xAl_x) O_{10} $(OH)_2{\cdot}nH_2O$ and in trioctahedral form expressed as M_x (Mg_3) (Si_4–xAl_x) O_{10} $(OH)_2{\cdot}nH_2O$.

The interlayer position contain two distinct sheets of water and the water molecules in each sheet are arranged in a near hexagonal pattern (Espantaleon, Nieto *et al.* 2003).

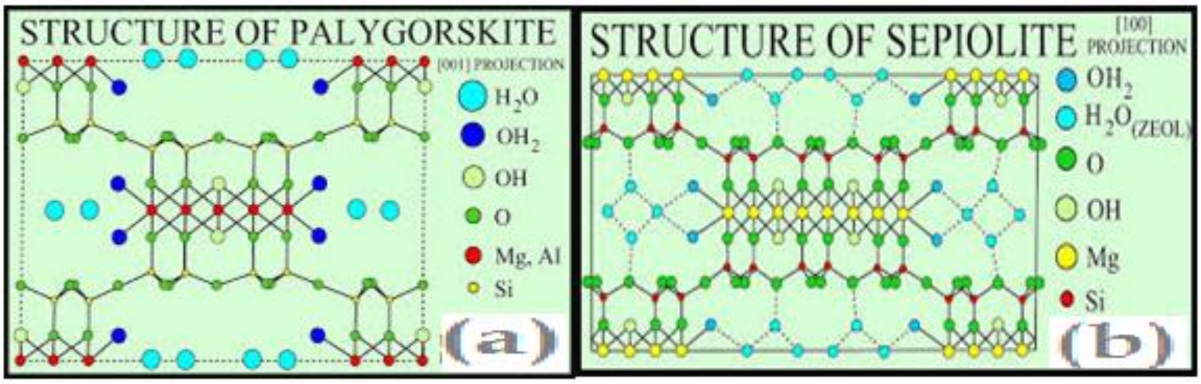

Fig. 13. Molecular structure of (a)Palygorskite, (b) Sepiolite.

Structure of Vermiculite clay

The Mg molecules are present between the water sheets and bonded octahedrally with water molecules. The cation exchange capacity of dry vermiculite nearly between 120 and 200 meq/100g. Vermiculite have ability to change the surface by organic and inorganic cation, to enhance its adsorbing capacity towards different pollutants.

Palygorskite and sepiolite

Palygorskite and sepiolite are natural clay mineral of magnecium hydrated silicate. Sepiolite is similar with palygorskite but sepiolite have large unit cell.

Palygorskite and sepiolite have light tan or cream to brown in color while some have a blue-green tint.
The general formula for sepiolite is $Si_{12}Mg_8O_{30}$ $(OH)_4$ $(H_2O)_4.8H_2O$ and for palygorskite is $Si_8Mg_5O_{20}(OH)_2(H_2O)_4.4H_2O$ (Liu 2007). These clays have porous structure, have more adsorbing capacity towards micro pollutants like metal cations and dye (Brown 1972). Palygorskite and sepiolite have more adsorbing capacity towards agricultural wastes. Both clay minerals are Mg silicates but Palygorskite shows additional structural diversity and contain less Mg and more Al than sepiolite (Yua and Han 2015).

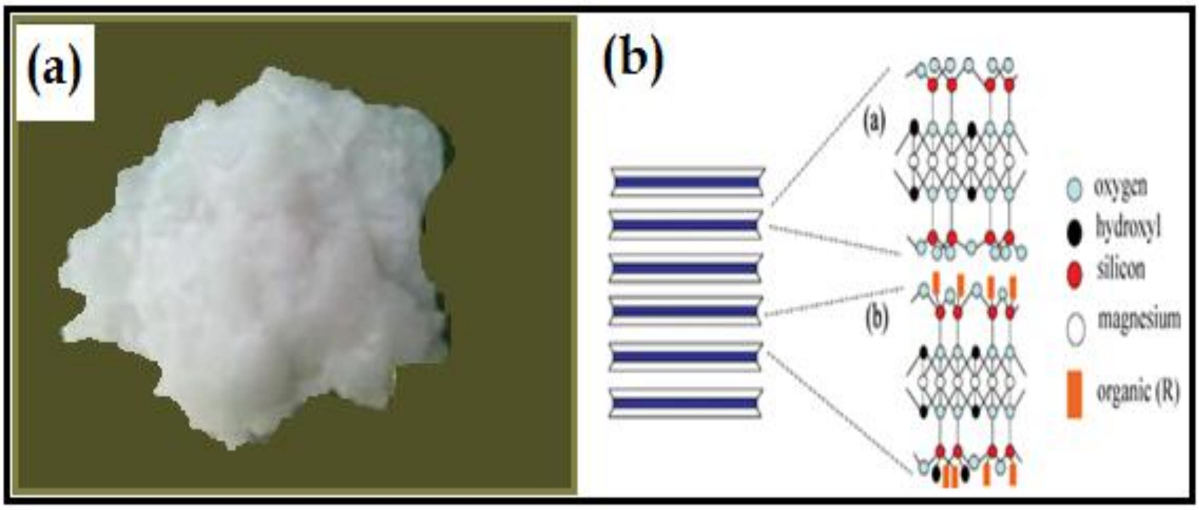

Fig. 14. (a) Physical appearance of Hectorite (b) Molecular structure of Hectorite.

These clays are not swell on exposure to water and form irregular lattices that have capacity to captured water which give them to gelling property and suspend on the surface of water.

These two clays are stable at high temperature, and are not effected by electrolytes and are applicable for many uses (Murray 2002).

Hectorite

Hectorite is a smecite natural clay mineral (Estévez, Arbeloa *et al.* 1995). It is a 2:1 trioctahedral smecite clay that is consist on one octahedral sheet of Mg enveloping in between the two tetrahedral sheet of silica. Hectorite have general formula M_x $(Mg_{3-x}Li_x)$ (Si_4) O_{10} $(OH)_2*nH_2O$. It has enduring a negative charges that arise due to the isomorphous substitution of Li^+ for Mg^{2+} (Luckham and Rossi 1999). Hectorite are rare clay adsorbent that are limited in use. By cation exchange mechanism, make the hydrophilic surface of clay to organophilic (Özcan, Erdem *et al.* 2004). Modified surface of hectorite have adsorption capacity towards anionic dye.

Mechanisms of adsorption of pollutants on the surface of clay

The interaction between the clay and the organic pollutants depends on the structure and stability of organo clay complexes and the types of bond present between them (Theng 1974, Yariv 1996).

The interaction between the pollutants and the adsorbents is due to physical forces as well as chemical forces. The physical forces that adjusting adsorption by Van der Waals forces, hydrophobicity, hydrogen bonds, polarity and steric interaction, dipole induced dipole interaction, π-π interaction etc.

In physical adsorption the pollutants are collect on the surface of adsorbents by physical forces.

For example, the high molecular weight poly ethylene oxide (PEO) adsorbed on silica involved hydrogen bonding and when adsorbed on silanol groups involved hydrophobic interaction (Rubio and Kitchener 1976). Generally, the adsorption capacity of the adsorbent depends on the concentration of water molecules that are present in the pores. Some adsorbent such as activated carbon show more capacity or demonstrated superior adsorption property.

It has been revealed that the primly adsorbed low molecular weight pollutants are replaced by high molecular weight pollutants. Consequently, activated carbon certainly adsorbed propane as compare to methane (Tinge, Mencke *et al.* 1987). The efficiency of adsorption increases with the increase of surface area of adsorbent at a given temperature. The adsorbent showed effectiveness due to the enhancement of the adsorbent area at a given temperature.

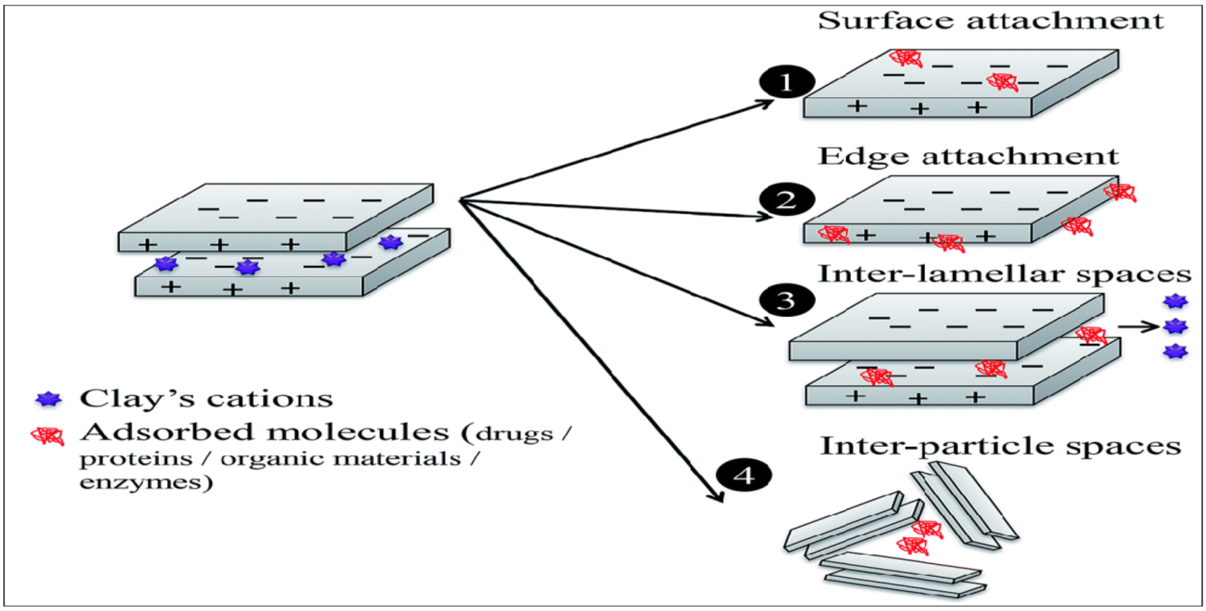

Fig. 15. Mechanism of adsorption of pollutants on the surface of clay.

In chemisorption, there is a chemical bond formed by the sharing of electrons between the pollutants and the surface of adsorbents. For example, activated carbons have ability to disintegrating numerous pollutants including oxides of nitrogen, silver salt solutions, halogens etc (Puri, Singh *et al.* 1965, El and Al-Hazmi 2015). With the help of carbon-oxygen bond, adsorption takes place in all these above adsorbents. The nature and the amount of carbon-oxygen bonds is the function of temperature, pressure surface area, nature of carbon surface and oxidative methods. For instance, in acidic carbon-oxygen surface groups are very well know and easily established by reaction with oxidizing solution at room temperature or at temperature of 400°C. Neutral carbon-oxygen surface group are more stable as compared with acidic surface group, and start decaying at temperature range extent from 500-600 °C and these are removed completely. The 2:1 clay minerals might undergo grafting reactions, because of the presence of silanol and aluminol groups on surface that react with organic contaminants. Grafting reactions are those reactions in which covalent bond established between reactive surface groups and organic contaminants [(Nourmoradi, Avazpour *et al.* 2016).

Adsorption of dyes on clay surface

Dye is the Major pollutant that are predictable in wastewater (Banat, Nigam *et al.* 1997). At very low concentration of dyes in water (less than 1 ppm for some dyes) is highly toxic and undesirable (Robinson, McMullan *et al.* 2001). Dyes are extensively used in industries such as textiles, rubber, paper, plastics, cosmetics, etc., to dye their products. Dyes are difficult to de-colorize because they resist to degrade on exposure to light, water and many chemicals because of their chemical structures, the colour diminishes aquatic life by blocking the way of sunlight through water. The main source of dye pollution is textile wastewater comes from dyeing processes, (Al-Degs, Khraisheh *et al.* 2000). Also, some dyes might be toxic to various organisms (Khattri and Singh 1999). Currently the adsorption technique have been demonstrated to be an effective and attractive process for the adsorption of dyes from wastewaters (Khenifi, Bouberka *et al.* 2007, Ma, Shek *et al.* 2008).

Gao. Y *et al.*, used iron modified bentonite clay adsorbent for the removal of carcinogenic dye (Rhodamine B, RhB). Iron modification enhanced the adsorption property of the bentonite, effortlessly detached from the treated solution and regenerated by the visible light photo-Fenton process. The adsorption capacity of iron modified bentonite (FeMB) was approximately 168.13 mgg^{-1}. Adsorption capability of adsorbent is restored and is more significant, safely discarding the organic pollutants (Gao, Guo *et al.* 2016). Chinoune. K *et al.,* used bentonite that are modified by covered with Magnesium hydroxide B–Mg $(OH)_2$, enhanced its adsorption capacity towards anionic reactive dyes: Procion blue HP (PB) and Remazol brilliant blue R (RB). The presence of electrolytes and large amount of other anions decreasing the adsorption efficiency of adsorbents. At pH = 2, the maximum adsorption of RB was 98.2% and 87.8% PB was found (Chinoune, Bentaleb *et al.* 2016). Anirudhan. T. S and Ramachandran. M studied the adsorption of Basic dyes from water with the help of surfactant modified clay bentonite by applying binary component system. Adsorption of dyes on the surface of clay was completed within 240 minutes. Equilibrium adsorption data followed Freundlich model and pseudo second-order well defined the kinetics. HYBRID error investigation were applied to adequate the kinetics and isotherms models (Anirudhan and Ramachandran 2015). Makhoukhi. B *et al* investigated the adsorption of Telon dyes by Bentonite modified with ortho, meta and para bis-imidazolium salts, from water by applying Batch adsorption technique.

The modified bentonite was observed through infrared spectroscopy, X-ray diffraction and thermogravimetric analysis. Telon dyes are synthetic textile dyes which include Telon-Orange, Telon-Red and Telon-Blue that was removed by adsorption process. The kinetic data followed pseudo-first order equation and equilibrium adsorption isotherm was best described by Freundlich and Langmuir isotherms of adsorption (Makhoukhi, Djab *et al.* 2015). Aguiar. J. E *et al* studied the adsorption of reactive dyes Remazol Violet 5R and Acid Blue 25 on porous clay hetrostructure that was synthesized with bentonite. The adsorption process was conducted in a stirred tank to calculate the effect of contact time, pH and initial dye concentration.

The adsorption equilibrium data was well pronounced through Langmuir-Freundlich isotherm. Electrostatic interactions occurring between the silanol groups of the clay and amine or hydroxyl groups of the dyes (Aguiar, Cecilia *et al.* 2017). Toor. M *et al* recognized the low cost and efficient activation procedure for enhancing the adsorption ability of Australian Bentonite help in removing toxic pollutants like Congo-Red dye from waste water.

Three activation procedures were used including thermal activation (TA),acid activation (AA), and combined acid and thermal activation (ATA). Thermal activation carried out at 100 C for 20 min which showed more than 20% increase in surface area. However above 100 C exhibited a decrease in surface area due to degeneration of the crystal structure.

The ATA activation process enhance surface area, pore size and modify the morphology of raw bentonite more than TA and AA activation process. So the activated bentonite have more adsorption capacity of Congo-Red from waste water (Toor, Jin *et al.* 2015). Zohra. B, adsorbed Benzopurpurin 4B (Direct Red 2) on bentonite that was modified by quaternary ammonium organic cations. Direct Red 2 is an azo dye, which comprises two nitrogen, bonded with each other through double bond (N═ N and a sulfonic group (NaO_3S). Due to the presence of sulfonic group dye dissolved in aqueous medium. CTAB-Bentonite is an effective and extensively used cheap adsorbent for removing Direct Red 2. There was two types of forces existed between the CTAB- Bentonite and Direct Red 2 dye.

1. There was a strong mode of interaction between the sulfonic group and positively charged surface clay adsorbent that was due to the presence of CATB.

2. The second mode of interaction present between the clay and dye is hydrophobic interaction (Zohra, Aicha *et al.* 2008).

A. Khenifi *et al.*, investigated the adsorption of Supranol Yellow 4GL (industrial dye) on cetyltrimethylammonium bentonite modified clay surface. Supranol Yellow 4GL (anionic dye), which is not adsorbed on negatively charged bentonite surface. So bentonite surface is modified by replacing cetyltrimethylammonium cations (CTAB) with inorganic ions. It is effected by following parameters like concentration of adsorbate and adsorbent, contact temperature and pH. Adsorption of Supranol Yellow 4GL depends on the concentration of CTAB and the adsorption of Supranol Yellow 4GL is maximum at acidic pH and high temperature *(Khenifi, Bouberka et al.* 2007). Alex Chi-Kin Yip *et al.*, used heterogeneous acid activated Cu/clay adsorbent which act as a catalyst. This was prepared by dispersing the copper onto the surface of bentonite by chemical vapour deposition (CVD). The copper was detached from the clay surface which is problematic for human health. To overcome this problem first the bentonite was washed with H_2SO_4. The adsorption properties of the Cu/acid-activated clay play an important role in the catalytic reaction at a wide range of pH. This adsorbent is used in removing the textile dyes from waste water in the presence of UV radiations and H_2O_2 (Yip, Lam *et al.* 2005). Liu. B *et al.*, prepared organo-montmorillonite by using Gemini surfactants and irradiated with microwave for 1 h. The Gemini surfactant enhanced montmorillonite structure morphology than cetyltrimethyl ammonium bromide surfactant. By microwave irradiation method produced larger interlayer spacing in organo-montmorillonite. The hydrophobicity and surface area of organo-clay gradually increased with the increase of the chain length and amount of the surfactants. This modified organo-clay exhibited better remarkable adsorption capacity for methyl orange dye than MMT (Liu, Wang *et al.* 2011). Acisli. O *et al* studied the adsorption of Acid Red 17 dye in the presence of ultrasound waves by modified nanosized montmorillonite clay with dodecyltrimethylammonium bromide. Modification of clay with dodecyltrimethylammonium bromide, it increases the surface area of clay from 19.76 to 42.57 m2/g and interlayer space increased from 1.13 to 1.69 nm. The Ultrasound waves enhanced the adsorption capacity of the organo-montmorillonite through immediate adsorption and sonocatalysis. The adsorptiotion performance of modified clay was slightly effected by initial adsorbate concentration, pH and by inorganic anions (Acisli, Khataee *et al.* 2016). Aydin Hassan *et al.,* used Nano-sized montmorillonite(MMT)/calcium alginate(CA) adsorbent to adsorb a textile dye from aqueous solution. The reusability test specified that immobilized clay might be used as an efficient adsorbent for removing textile dye in repeated adsorption–desorption cycles. The maximum adsorption of basic red 46 (BR46) depends on initial concentration of dye and adsorbent dosage, temperature and contact time (Hassani, Soltani *et al.* 2015). Chun-Hui Zhou *et al.*, used cellulose acetate/organo-montmorillonite (CA/OMMT) composites in removing the Acid Scarlet G (ASG) anionic dye from waste water. Cellulose acetate/organo-montmorillonite (CA/OMMT) composites were prepared by mixing cellulose acetate (CA) and organo-montmorillonite (OMMT) and then dispersed in acetone, followed by evaporation and drying, to get paper-like cellulose acetate/organo-montmorillonite (CA/OMMT). The adsorption of ASG onto CA/OMMT depends on adsorption time, temperature, pH of dye solution, and as well as initial concentration of dye. Adsorption process is an endothermic and spontaneous process. It follow Lagergren's pseudo-first-order kinetics and adsorption isotherms was fitted into Langmuir equation (Zhou, Zhang *et al.* 2012). Faiza Zerman *et al.*, used iron surfactant-modified pillared montmorillonite (Fe-SMPM).The attractive adsorbent was prepared by introducing the iron in the interlayer spaces of montmorillonite to formed pillared montmorillonite and then was modified by surfactant cetyltrimethylammonium bromide (CTAB) which increase its hydrophobic character. The iron surfactant-modified pillared montmorillonite adsorbed basic yellow 28 dye (BY28) and 4-nitrophenol (4-NP) at different pH values both in single component and binary pollutant systems. In single system Fe-SMPM have more attraction towards basic yellow 28 dye (BY28) as compared to 4-NP but in binary component system 4-NP sorption capacity onto Fe SMPM increased when the BY28/4-NP ratio increased (Zermane, Bouras *et al.* 2010). Almeida. C. A. P *et al* studied the adsorption of cationic dye on montmorillonite clay adsorbent through batch adsorption technique. Adsorption equilibrium of dyes on clay surface was best described by Langmuir isotherms. Thermodynamic analysis showed adsorption is endothermic and spontaneous. It followed intra particle diffusion model, pseudo first and second order kinetics but its adsorption kinetics was best defined by pseudo second order kinetics (activation energy +28.5 kj mole) (Almeida, Debacher *et al.* 2009). Tian. G *et al* investigated the adsorption of dye on activated palygorskite clay in the presence of ammonium sulfide. Clay was activated by using hydrothermal process, enhanced the distribution of clay particles which created more negative charges on clay surfaces and established a novel place for adsorption. The adsorption capacity of activated palygorskite clay was 156.05 to 218.11 mg/g. The adsorption kinetics data was well explained by pseudo second order and equilibrium isotherms and followed Langmuir adsorption equation. Adsorption process involved electrostatic interactions and chemical bond occur between adsorbate and clay surface (Tian, Wang *et al.* 2016). Moreira. M. *et al* organized two fibrous clay minerals palygorskite and sepiolite that was modified by grafting them with amine groups (3-aminopropyl) triethoxysilane, improves the adsorption capacity towards Methylene Blue (cationic dye) and Mentanil Yellow (anionic dye). Metanil yellow has a carcinogenic effect and effects animals and human beings. Grafted organic compounds contained different functional groups and have different affinities towards organic and inorganic pollutants (Moreira, Ciuffi *et al.* 2017). Bingol. D *et al* studied the adsorption of dye on sepiolite clay adsorbent through batch adsorption technique by using a full factorial design. Adsorption of dyes on clay depends on pH, temperature and ionic strength of solution (Bingol, Tekin *et al.* 2010). Araceli Rodrı´guez *et al* investigate the adsorption of Methylene Blue dye on two clays adsorbents, sepiolite and pansil. The maximum Methylene Blue adsorption was achieved for sepolite (at acidic pH) and pansil (at basic pH). The adsorption of MB on two clays was well defined by Sips isotherms. The adsorption mechanisms consist of two stages. In stage I, adsorption occur at the surface while stage II corresponds internal diffusion (Rodríguez, Ovejero *et al.* 2010). Stawiński. W *et al* studied the adsorption of dyes and metals ions by activated vermiculite. The vermiculite was activated through acid, alkaline and mixed acid/alkaline treatment, to enhance its adsorption capacity. Adsorption capacity of clay followed given sequence: raw vermiculite have less attraction towards dye and metals ions, acid/base treated vermiculite have more adsorption capacity towards dyes as compared to metal ions that was well adsorbed by base treated vermiculite. The adsorbent was regenerated and used in some sorption processes. It was probable to isolated adsorbed dyes from metals ions, by treated with Ethanol/NaCl solution and 0.05 M HNO_3 (Stawiński, Węgrzyn *et al.* 2017). Xubiao Yu *et al* used the organically modified vermiculite as an adsorbent for removing anionic dye (congo red) from waste water. Vermiculite is organically modified with hexadecyl trimethylammonium bromide (HDTMAB). The adsorption capacity of organo-vermiculite is greater than vermiculite by increasing the HDTMAB. The results from adsorption isotherm shows that the adsorption of CR increasing by increasing the temperature. . The thermodynamic parameters specifies that CR adsorption onto organovermiculite was endothermic and spontaneous in nature. So organovermiculite, an effective adsorbent for the adsorption of anionic dye (congo red) from pollutant water. The kinetic experimental result shows that it follows the pseudosecond-order kinetic model and were well defined by the Langmuir model (Yu, Wei *et al.* 2010). Unuabonah. E. I *et al* investigated the kinetics and single batch sorber design for the adsorption of Aniline Blue dye on the surface of adsorbent sodium tetraborate kalonite clay. Sodium tetraborate enhanced the adsorption capacity of clay from 1666 to 2000 mg/kg. Sodium tetraborate Kaolinite clay was best defined by Langmuir isotherm model and there is homogeneous adsorption of dye on the modified clay surface. Equilibrium kinetics data was well explained by second order kinetics. Initial sorption rate and dye concentration are inversely related (Unuabonah, Adebowale *et al.* 2008). Baskaralingam. P *et al* used modified adsorbent hectorite used for the adsorption of C.I Acid Red dye 151 (acidic dye) from waste water. The cationic surfactant changed the clay from hydrophilic to organophilic. Hectorite was modified by two cationic surfactant cetyldimethylbenzylammonium chloride and cetylpyridinium chloride. The modified cetyldimethylbenzylammonium chloride-hectorite (CDBA-hect) had adsorption capacity 208.33 mg g_{-}^{1} and cetylpyridinium chloride (CP-hect) have 169.49 mgg−1.. The experimental data showed that maximum adsorption occur at acidic pH (Baskaralingam, Pulikesi *et al.* 2006). Gupta. V. K *et al* used nontronite clay mineral as an adsorbent for removing two anionic azo dyes specifically napthol red-J and direct orange through batch adsorption mode. Nontronite is a clay mineral and its structure is composed on octahedral iron as opposed to octahedral aluminum or magnesium. The empirical formula of nontronite is $Na_{0.3}$ Fe^{3+} $_{2}Si_{3}$ AlO_{10} $(OH)_{2}$. 4(H2O) with molecular weight of 495.90 g. Another name of nontronite is chloropal. Adsorption was depended on pH of solution and temperature. Adsorption of two dyes have direct relation with temperature and inverse relation with pH (Gupta, Mohan *et al.* 2006). Hassani. A *et al* investigated the adsorption of cationic dyes on modified nano-clay from aqueous medium enhanced by applying central composite design. The particle size of nano-clay was approximately 16.5 nm. The adsorption of dyes on nano-clay depends on dye and clay concentration, pH and contact time. Precision of model and worsening coefficients was evaluated by means of analysis of variance. The optimum condition that was composed by central composite design, progress the adsorption of dyes on nono-clay adsorbent (Hassani, Khataee *et al.* 2015). Bhattacharyya. R and Ray. S. K was removed two dye, Congo red and Methyl violet by adsorption on nano clay composites that was filled with hydrogels of acrylic acid and polyethylene glycol. These modified hydrogels was showed high swelling results and have adsorption capacities of dyes. The Congo red was highly adsorbed on modified clay than Methyl violet because of difference in their molecular structure. The adsorption was exothermic in nature (Bhattacharyya and Ray 2015). Gil *et al.*, used two pillared clay adsorbent that was synthesized by intercalated the solution of aluminium and zirconium in the interlayer space of the clay. The aluminium and zirconium clearly modified the surface property of the pillared clay. The whole surface of the clay carried negative charge. . Both clays have the same adsorption capacity for Orange II whereas the adsorption ability of Zr-PILC was greater than Al-PILC for Methylene Blue. There is an electrostatic attraction between the negatively charged surface clay and positively charged dye Methylene Blue. But in case of Orange II which is an anionic dye, so there is a repulsion between the two opposite charged surfaces. By introducing NaCl which enhanced the adsorption capacity of both the pillared clays towards Orange II (Gil, Assis *et al.* 2011). Mouloud Lezehari *et al* used gel-beads as an adsorbent for removing organic pollutants from water. Gel-beads adsorbents was prepared by crosslinking between Sodium alginate and Aluminium pillared clay or modified pillared clay with surfactant (CTAB-Al-Mont-PILC). The encapsulation of clays into alginate beads which modified its surface morphology and enhance its adsorption capacity. They used this type of adsorbent in removing pentachlorophenol (neutral/anionic biocide) and safranine (cationic dye) from waste water (Lezehari, Basly *et al.* 2010). Xiaorong Zhao *et al* modified the clay mineral rectorite by iron, which is used both as an adsorbent and as a catalyst. The bifunctional material is acting both as an adsorbent and photocatalyst in removing the organic contaminants from water. Iron-modified rectorite (FeR) is used to remove tracer dye like Rhodamine B (RhB) from water. First RhB adsorbed on the FeR and then catalyzed by FeR in the presence of sunlight and H_2O_2. FeR have high chemical stability and working over a wide range of pH (Zhao, Zhu *et al.* 2012). H.Y. Zhu *et al* synthesized highly porous adsorbent which act as a photocatalyst help in degradation of organic contaminants from water. This is synthesized by the reaction between the acidic solution of titanium hydrate and the clay in the presence of surfactant poly (ethylene oxide) (PEO). The TiO_2 Nanoparticles that are introduced in the interlayer space of the clay and replace the Mg or Al ion from the clay which provided a wide space for the organic contaminants. The surfactant PEO increase the surface area and porosity of the clay adsorbent. This solid adsorbent is an effective photocatalyst help in the degradation of phenol and synthetic dyes from waste water (Zhu, Li *et al.* 2005).

Adsorbing pharmaceuticals products like antibiotics and antidepressant drugs

Antibiotics are widely used in large quantities for humanoid infection medicine, veterinary medicine and husbandry growth promoters. Due to incomplete metabolization of these drugs in human or animal body, these are excreted through urine and feces. As a result of the agricultural application of manure and sewage sludge containing un-metabolized drugs, wastewater irrigation and the throwing away of domestic and hospital waste, they are readily discharged into water through different pathways (Halling-Sørensen, Nielsen *et al.* 1998). Presently, they were commonly identified in municipal wastewater, shallow water, ground water, soils and sediments (Daughton and Ternes 1999, Giger, Alder *et al.* 2003). These are long-term risks to human and ecological health (Levy 1998).

Saitoh. T and Shibayama. T studied the adsorption and degradation f an antibiotics on surfactant modified montmorillonite clay adsorbent from water. Adsorption efficiency of modified clay increases towards antibiotics with increasing the loadings of surfactant ions on clay surface. Degradation efficiency increases with increasing the temperature (Saitoh and Shibayama 2016). Bo Liu *et al* enhanced the adsorption capacity of clay adsorbent montmorillonite by the addition of ester-containing Gemini surfactant in the presence of micro-wave irradiation. The surface of the ester-containing Gemini surfactant-modified MMT (EMMT) is hydrophobic, feathery and coarse which have more adsorption capacity. There was an electrostatic interaction between ester-containing Gemini surfactant and MMT. The maximum adsorption volume was up to 133 mg/g. EMMT adsorbed organic pollutant triclosan (TCS) more than simple montimorillonite. The adsorption of triclosan (antibacterial) on EMMT surface is monolayer and was well described by Langmuir isotherm model (Liu, Lu *et al.* 2014). Qingfeng Wu *et al* used two clay minerals as an adsorbent, montmorillonite (SAz-1) and kaolinite (KGa-1b) for removing quinolone antibiotic, nalidixic acid (NA). The adsorption of NA on clay minerals highly depend on pH of solution. When pH of solution is below its pKa value, then there is a hydrophobic interaction between the clay minerals and NA. But when the pH of the solution is above its pKa value, then there is an electrostatic interaction is responsible for the adsorption of NA on clay mineral (Wu, Li *et al.* 2013). Avisar. D *et al* explored the adsorption of antibiotics sulfadimethoxine, sulfamethoxazole, tetracycline and oxytetracycline on the surface of montmorillonite in the presence of synthetic effluents, waste water effluents and humic acids. At environmental pH, sulfadimethoxine and sulfamethoxazole low sorption capacity towards clay while tetracycline was highly sorbed on clay. The adsorption of organic pollutants have different sorption capacity because of their difference in molecular structures and due to the presence of divalent cations in effluents. Adsorption isotherm of tetracycline was best pronounced by Freundlich model (Avisar, Primor *et al.* 2010). Berhane. T. M *et al* was demonstrated the adsorption of endocrine-disrupting compound, Bisphenol A, and the antibiotic ciprofloxacin on palygorskite-montmorillonite particles and adsorption was highly depended on temperature, nature of solution and granules size. The experimental data was described by Langmuir isotherms and the adsorption was spontaneous was showed by thermodynamic analysis. The smallest or intermediate granules were suitable for removing Bisphenol A and ciprofloxacin from pollutant water. Ciprofloxacin adsorption was highly depended on pH of Bisphenol A, and was slightly depended on ionic strength and pH. Sorption of both compounds on granules were designated as the sorption process was an irreversible (Berhane, Levy *et al.* 2016). Tsai. Y. L *et al* used palygorskite clay (PFl-1) to removed Amitriptyline (AMI) which is a tricyclic antidepressant medicine. Palygorskite is a magnesium-aluminum phyllosilicate, have a fibrous structure and have a large enough space to accommodate an organic pollutants. The adsorption capacity of palgorskite clay (PF-1) was 0.168 mmolg $^{-1}$ at pH 6-7 and AMI adsorption was fast on clay surface and was reached to equilibrium within 15 min (Tsai, Chang *et al.* 2016). Chang. P. H *et al* studied the adsorption of antibiotics Ciprofloxacin, phenylpiperazine and fluorochloroquinolone carboxylic acid on palygorskite clay. The adsorption of these compounds was best described by Langmuir model at pH 2, 7, and 11 while fluorochloroquinolone carboxylic acid at pH 2. The adsorption capacities of Ciprofloxacin, phenylpiperazine were 98–160 mmol/kg. The adsorption occurred through cation exchange mechanism. The FTIR analysis confirmed strong interaction bew the clay surface and adsorbed compounds (Chang, Jiang *et al.* 2016). Sturini. M *et al* was investigated to adsorbed Fluoroquinolone drugs e.g. Marbofloxacin and Enrofloxacin pollutant from wastewater on sepiolite clay and was regenerated by photo induction.

The adsorption was observed only on the external site of the clay, not in the interlayer spacing, there is an interaction occurring between the carboxylic group of fluoroquinolone and on clay surface. The sorption experimental data was best pronounced by Freundlich, Langmuir and S-logistic 1 models. Adsorbed drugs were successfully photodegraded with solar light, consequently allowing the sepiolite to be regenerated (Sturini, Speltini *et al.* 2016). Arya. V and Philip. L investigated the adsorption of some Pharmaceuticals on magnetic clay composites. Surface area of modified clay was 94.81 m²/g and have a large porous structures. Kinetics of adsorption was best defined through pseudo second order and equilibrium adsorption data equilibrium followed Freundlich equation. There is an electrostatic interactions between the adsorbate and a clay surface. The adsorption was effected by pH and humic acid. Modified clay was easily separated from the solution because of its magnetic behavior (Arya and Philip 2016). Oliveira. T. D *et al* studied the adsorption of pharmaceutical yields Diclofenac on modified clay adsorbent. Adsorption depends on dosage surfactant ions temperature and pH of solution. There is an electrostatic interaction between the clay and Diclofenac. There is a hydrophobic complexes occur between diclofenac and modifying agent that enhance the adsorption and intercalation of pollutants on organo-clay surface. Equilibrium adsorption isotherms followed Langmuir, Freundlich and Dubinin–Radushkevish equation (De Oliveira, Guégan *et al.* 2017). Shakir. K *et al* was removed an antiseptic organic contaminant Catechol by adsorbing on organo-bentonite from wastewater by using Batch adsorption technique. The adsorption behavior was depended on following parameters like contact time, temperature, pH and concentration. Equilibrium data and first order kinetics was well proscribed by frendulich and Langmuir adsorption equations. It was a spontaneous physisorption process.

Adsorption of herbicides

Herbicides are widely used to increase agricultural productivity (Azejjel, Ordax *et al.* 2010). A wide range of herbicides is introduced into the water from different sources like chemical spills, industrial effluents and agricultural run-offs. The discharge of contaminated water containing herbicides effects the environment. Clay minerals have large surface areas along with small particle size. After surface modification of clay with inorganic or organic cations, used as an adsorbents to many toxic herbicides (Hermosin and Cornejo 1992, Pal and Vanjara 2001). N. Jović-Jovičić *et al* was studied the adsorption of slightly hydrophobic herbicide ethofumesate on bentonite clay in the presence of different co-solvents like methanol, hexane and dissolved organic matter from aqueous solution. The clay surface was modified by adding long-chain quaternary ammonium ions like tetramethylammonium, octyl trimethylammonium and octadecyl trimethylammonium. The adsorption of ethofumesate was increased by increasing the carbon contents. Adsorption decreased 4–7-fold (TMA-clays), 3.2-fold (OTMA-clays) and 2.4–2.8-fold (ODTMA-clays) in the presence of methanol. Adsorption of herbicide was enhanced by the presence of co-solvents on modified clay (Jović-Jovičić, Milutinović-Nikolić *et al.* 2010). Jianfa Li *et al* synthesized novel organic-inorganic bentonite by co-adsorption of cetyl trimethylammonium (CTMA) ions and poly(hydroxo aluminum) or poly(hydroxo iron) cations, for the removal of ionic herbicide 2,4-dichlorophenoxyacetic acid and non-ionic herbicide Acetochlor (2-chloro-N (ethoxymethyl)-N-(2-ethyl-6 methylphenyl) acetamide). Organic-inorganic bentonite have better adsorption capacity than simple bentonite. There is a van der Waals interaction between the nonionic herbicides and modified clay (Li, Li *et al.* 2009). Ding. C *et al* prepared Chitosan–montmorillonite bionanocomposite (CTS–MMT) to adsorbed herbicide quinclorac (QC) from waste water. CTS–MMT adsorbent have more adsorption capability towards QC than unmodified montmorillonite. QC strongly adsorbed on CTS–MMT adsorbent by electrostatic attraction, hydrogen bonding, van der Waals interactions and cation-dipole, and QC was not desorbed by water molecules but only desorbed by 0.1 mol/L solution of NaOH. QC have adverse effects on aquatic life beside this it is hepatic and renal toxicant (Ding, Gong *et al.* 2016). Santiago. C. C *et al* was adsorbed and characterized a contaminated herbicide 4-chloro-2-methylphenoxy acid on modified montmorillonite clay. Clay was organically modified with loading of Dodecyl trimethyl ammonium. 4-chloro-2-methylphenoxy acid was adsorbed on organo-montmorillonite approximately 3 times greater as compared to raw montmorillonite. The agglomerates was formed through organo-montmorillonite after the retaining of 4-chloro-2-methylphenoxy acid, this was an easier way to separate the solids from the aqueous medium by simple technological process (Santiago, Fernández *et al.* 2016). Park. Y *et al* removed two herbicides imazaquin and atrazine using montmorillonite that was modified through ion-exchange method with organic cations. Organo-clay adsorbed anionic imazaquin through strong hydrophobic and electrostatic interaction on the outer surface as well as in the inner surface of MMT. Organo-clays are not possibly a good adsorbents towards atrazine but the adsorption of atrazine is significantly enhanced, when the mixture comprising both imazaquin and atrazine. This phenomenon is described as a synergetic effect (Park, Sun *et al.* 2014). Brown. J. L. M *et al* was investigated the adsorption kinetics of Picloram (synthetic herbicide) on montmorillonite clay surface in situ by ATR and FTIR analysis. They applied different rate and mass transfer equation for studying kinetics and proposed that the adsorption n processes are controlled by intra particle diffusion. They proposed anionic bonding and a complex formation mechanism between nitrogen and carboxyl group for the adsorption of picloram on clay surface (Marco-Brown, Areco *et al.* 2014). M. Mekhloufi *et al* compared the adsorption capability of three clays, Sodium montmorillonite (Na-M), acidic montmorillonite (H-M), and organo-acidic montmorillonite (Org-H-M). Sodium montmorillonite (Na-M) was the original clay, acidic montmorillonite (H-M) was prepared by the intercalation of an acid while the organo clay was prepared by intercalation of cationic surfactant ammonium acetate. These clays was used to remove herbicide 8-quinolinecarboxylic acid (8-QCA) from waste water. The adsorption of 8-QCA decreased in the order Org-H-M > H-M > Na-M. 8-QCA is herbicide and are highly toxic pollutant. The organo-clay have greater adsorption capacity than other clays because the surfactant molecule increased the surface area and porosity of the clay and it also provide a new external site on the clay surface for pollutants

(Mekhloufi, Zehhaf *et al.* 2013). Bouras Omar *et al* used surfactant modified pillared montmorillonites adsorbent for adsorption of herbicides. Actually they used three type of SMPM adsorbent. Pillared clay montmorillonites was prepared initially by replacing the interlayer space of montmorillonite with metallic polycations of aluminum (III), iron (III) or titanium (IV) and then was modified by surfactant molecule cetyl trimethylammonium bromide. The efficiency was in the order: $CTA\text{-}Ti_x\ H_y$ -montm > $CTA\text{-}Fe_x(OH)_y$-montm > $CTA\text{-}Al_x(OH)_y$-montm. The organic-inorganic montmorillonite have ability to adsorbed herbicide diuron and its degradation products (Bouras, Bollinger *et al.* 2007). T Polubesova *et al* Removed herbicides by montmorillonite that was enhanced by intercalation of micelles (octadecyltrimethylammonium and benzyldimethylhexadecylammonium) from aqueous. In adsorption of herbicides, micelles critically depends on the nature of organic cationic headgroups. Column-fillter techniques was used that was consisted on the mixture of sand quartz and benzyldimethylhexadecylammonium micelle clay complex removed approximately 99% herbicides contiminants. Micelle based clay complexes is an effective adsorbent for decontamination of water from organic pollutants (Polubesova, Nir *et al.* 2005). Sheng. G *et al* was adsorbed 4, 6-dinitro-o-cresol and 4, 6-dinitroo-sec-butyl phenol herbicides by smectite montmorillonite clay. The 4, 6-dinitro-o-cresol was adsorbed firstly as a neutral species and arranged parallel to the surface of clay. Lower hydrated cations like K^+ and Cs^+, have better adsorption capacity as compared to strongly hydrated cations, e.g. Na^+ or Ca^{2+}. Lower hydrated cations was directly interacted with $-NO^2$ group of 4, 6-dinitro-o-cresol and established an optimum interlayer spacing between 12 to 12.5 A^o while strongly hydrated cations established a greater interlayer spacing approximately greater than 15A^o was less interacted with $-NO^2$ group. Steric constraints was observed during 4, 6-dinitro-o-cresol adsorption that contained a methyl group as compared to 4, 6-dinitroo-sec-butyl phenol contained a bulkier isobutyl group (Sheng, Johnston *et al.* 2002). Paul. B *et al* used a modified beidellite clay adsorbent for herbicides, it was first activated with acid and then grafted with silane coupling agent to enhance its adsorbent capacity towards anionic imazaquin and non-ionic alachlor herbicides from water. Grafting provided a more hydrophobic sites on the surface of beidellite that enhanced its adsorption capability. Beidellite clay is a type of smectite clay mineral and the silane coupling agent that are used are 3-chloro-propyl trimethoxysilane or triethoxy silane (Paul, Martens *et al.* 2011). Shirzad-Siboni M *et al* Prepared, characterized and describe the application of a CTAB modified clay for the adsorption of an herbicide (bentazon) from waste water. The adsorption efficiency depends on quantity of adsorbent, pH and ionic strength of solution. Adsorption capability of samples were increased with Na_2CO_3 anion saturation, while in the presence of $NaHCO_3$, Na_2SO_4 and NaCl the adsorption capacity decreased (Shirzad-Siboni, Khataee *et al.* 2015). Celis. R *et al.* studied six different organic cations (L-carnitine, spermine, hexadimethrine, tyramine, phenyltrimethylammonium, and hexadecyltrimethylammonium) that was intercalated in the smecite clay minerals to adsorbed herbicides. These above organic cations enhanced the adsorption capacity of the clay towards herbicides. Modified clay adsorbent removed approximately 95% herbicides as compared to unmodified clay by using batch adsorption technique. The chemical properties of the organic cation significantly affected the adsorptive properties of the organoclay. The herbicides were reversibly adsorbed by the organo-clay (Celis, Trigo *et al.* 2007).

Adsorption of fungicides on various clay surface

Gamba. M *et al* removed synthetic fungicide Imazalil (IMZ) by using raw montmorillonite mineral that was obtained from Argentinean Patagonia and was enhanced by intercalating with different quantity of octadecyltrimethylammonium bromide loading. The role of ODTMA was to dislocate inorganic cations that exposed its interlayer space and facilitate IMZ interaction with the hydrophobic tetrahedral surface. ODTMA was a long chain alkyl group that increased the number of nonpolar sites which provided an effective interaction with organic pollutants. There was an electrostatic interaction between the siloxane surface of clay and IMZ (Gamba, Flores *et al.* 2015). Sánchez. R. M. T *et al* was demonstrated the adsorption of fungicide, Benzimidazole on thermally and mechanically modified montmorillonite clay. Thermal and mechanical treated montmorillonites exhibited a less adsorption capacity towards benzimidazole as compared to raw montmotillonite. Benzimidazole was provided different forms of nitrogen coordination surfaces. Protonated and deprotonated nitrogen have similar coordination capacity towards the surface of raw and thermally treated approximately 350°C montmorillonite while deprotonated Nitrogen have stronger coordination capacity towards thermally treated about 550°C sample. There is no nitrogen coordination but only cationic exchange was detected to the surface of mechanically treated montmorillonite (Sánchez, Genet *et al.* 2011). Cruz-Guzmaan, M *et al* modified the clay montmorillonite by natural organic cations ((L-carnitine, L-cystine dimethyl ester, and thiamine) for the adsorption of fungicides. These organic cations were introduced into the interlayer space of montmorillonite. The organic cations were designed on the basis of their origin and presence of diverse functional group in their structure. By batch adsorption experiment, the performance of clay in adsorption of fungicide were investigated. Batch adsorption results showed that modification with thiamine (Kf) 96-138), cystine dimethyl ester (Kf) 400-753), and especially carnitine (Kf >10 000) enhanced the adsorption of simazine by montmorillonite (Kf) 28-47). These natural organic cations enhanced much better adsorption capacity than the clay modified with alkyl ammonium cations (Cruz-Guzmán, Celis *et al.* 2004). Azarkan. S *et al* investigated the adsorption of metalaxyl and tricyclazole fungicides on natural Moroccan clays by means of the batch equilibration mode and clay was characterized through some techniques, thermal analysis, X-ray diffraction and measurement of surface area. Adsorption kinetics of metalaxyl and tricyclazole were successfully defined through pseudo second order model. Frendulich equation successfully described the equilibrium adsorption data (Azarkan, Peña *et al.* 2016). Liébana. J. A. R *et al* studied the sorption of fungicides on clay through Batch adsorption technique. Pseudo second order kinetics effectively applied and was best defined through Langmuir and Freundlich models. There is an electrostatic interaction between the fungicide and clay adsorbent. The adsorption of fungicide highly depends on organic content and granular sized of clay. This process was carried out at 10 and 20°C Temperature (Rodríguez-Liébana, López-Galindo *et al.* 2016). Jalil. M. E. R *et al* worked on aluminum clay mineral that was used to remove fungicide Thiabendazole from water. Adsorption of fungicide on aluminium clay, characterized through TGA, XRD and adsorption–desorption of N_2 at 77 K, NH_3-temperature programmed desorption and transmission electron microscopy. Adsorption of fungicides by batch adsorption technique was carried out at room temperature and at pH 6. Thiabendazol was physically and chemically adsorbed on the Al modified clay composite (Jalil, Baschini *et al.* 2014). Rodriguez-Cruz. M. S *et al* used layered and non-layered clay minerals as an adsorbent for fungiciedes penconazole and metalaxy and was modified by cationic surfactant, dihexadecyldimetylammonium (DHDDMA) that contain the two-chain alkylammonium organic cation and octadecyltrimethylammonium (ODTMA) and hexadecylpyridinium (HDPY) that are single chain organic cationic surfactant. Due to the presence of these large chain organic cations generate an organic barrier through the accumulation of their elastic alkyl chains that enhanced its sorption capacity towards non-ionic organic pollutants through hydrophobic interactions. These modified organo clays were used to sorbed two different hydrophobic fungiciedes penconazole and metalaxy (Rodríguez-Cruz, Andrades *et al.* 2008).

Adsorption of pesticides

Pesticides are the mixture of chemical compounds that are antiseptic and antimicrobial and are used for removing pests including insects, plant pathogens, weeds, birds, nematodes, and microbes that adversely affect the production, processing, storage, transport, or marketing of food or agricultural compounds (Dich, Zahm *et al.* 1997, Corsini, Liesivuori *et al.* 2008). Pesticides have severe effects on the human body and causing the following diseases: ataxia, paralysis, diarrhea, convulsions leading to muscle fibrillation, edema, dermatitis, dyspnea, irritability, hepatic microsomal enzyme induction, headache, peripheral vascular collapse, rhinorrhea, serum alkaline phosphate elevation, tinnitus, vomiting, and death due to respiratory failure. Allergic reactions include the following manifestations: anaphylaxis, bronchospasm, eosinophilia, fever, hypersensitivity pneumonia, sweating, pallor, pollinosis, sudden swelling of the face, eyelids, lips, and mucous membranes, and tachycardia. Continuing exposure effects in humans include choreoathetosis, hypotension, prenatal damage, and shock (Hallenbeck and Cunningham-Burns 2012).

Cruz-Guzmaan. M *et al* used functionalized organo-bentonite to adsorbed pesticides from waste water. The organo-clay was obtained by replacing the inorganic cations with natural organic cations, that contained appropriate polar functional groups (L-carnitine,L-cysteine ethyl ester,L-cystine dimethyl ester and thiamine) that is a beneficial approach to enhanced the clay performance towards specific pesticides, removed them from the environment. The organo-clay has selective adsorption capacity towards organophosphate pesticides and to catalyze their hydrolysis and thus decontaminate them from water. Organo bentonite clay having polar functional groups that have ability to enhance its adsorption capacity and selectivity towards pesticides, as most of the pesticides contained polar functional groups in their structure (Cruz-Guzmán, Celis *et al.* 2005). Pal, O.R and Vanjara, A.K compared three types of clay (bentonite, kaolin and montmorillonite) that are used as a adsorbent in removing the two pesticides malathion and butachlor. These clays was modified by three cationic surfactant molecule tetradecyltrimethyl ammonium bromide and cetylpyridinium chloride which replaced inorganic cations like Na^+ and Ca^{2+} to enhance its adsorption capacity by altering the surface from hydrophobic to organophilic. The adsorption of these pesticides per unit area on organo-clay is, TTA-Bentonite>TTA-montmorillonite>TTA-kaolin due to the presence of carbon amount in clay. The adsorption capacity of clay montomorillonite in removing the Malathion followed the order DTA (C_{12})-montmorillonite < TTA (C_{14})-montmorillonite < CP (C_{16})-montmorillonite. Butacholr is adsorbed more on the adsorbent than Malathion because of the higher hydrophobic nature of butacholar (Pal and Vanjara 2001). Bouras. O *et al* examined the consequence of humic acids on the adsorption of pentachlorophenol (pesticides) on surfactant modified montmorillonite clay. In a single system through batch adsorption isotherms, both pentachlorophenol and humic acid sorptions increased when pH decreased. The maximum pentachlorophenol sorption capability was 530 mg g^{-1}Vs 300 mg g^{-1}. Surfactant modified clay was thermally stable and efficient adsorbent towards organic pollutants. The adsorption of pentachlorophenol and humic acid was best described by Freundlich model (Bouras, Bollinger *et al.* 2010). Martin. M. J. S *et al* investigated the modification of montmorillonite clay minerals and observed its adsorption capacity towards different pesticides. Adsorption process was mostly effected by surface area, charge density and structure of the clay. Greater level of modification on the clay surface with surfactant ions, give rise the more hydrophobic character to the clay that attract the pesticides towards itself. The adsorption efficiency of modified montmorillonite was 100 times greater than raw montmorillonite towards pesticides (Sanchez-Martin, Rodriguez-Cruz *et al.* 2006).

Adsorption of phenolics compounds on clay

The different organic pollutants of aquatic ecosystems, phenols, especially the chlorinated ones, are one of the major organic pollutants subsequently they are harmful to plants, animals and human, although it is at low concentrations (Arellano-Cárdenas, Gallardo-Velázquez *et al.* 2005). Due to their extensive use, these compounds voluntarily enter into water, i-e by industrial and municipal waste water, by leachates come from waste deposits, by agricultural runoff of pesticides, by effluents from oil refineries, etc (Matthes and Kahr 2000, Yapar, Klahre *et al.* 2004). Residues of chloro-phenols have been found worldwide in soil, water and air samples, in food products, in human and animal tissues and body fluids (Troisi, Duarte-Davidson *et al.* 2004). Moreover, due to their slow degradation, chlorophenols, be a major hazard to ecosystems (Arellano-Cárdenas, Gallardo-Velázquez *et al.* 2005). Since chlorinated phenols are not biodegradation except at low concentrations, other methods such as chemical oxidation, coagulation, solvent extraction, liquid membrane permeation and adsorption are commonly used for their removal (Özbelge, Özbelge *et al.* 2002).

Richards. S and Bouazza. A was investigated the adsorption of Phenol on modified basaltic and bentonite clay surface. Batch adsorption technique was used for this purpose. Clay was organically modified with Hexadecyltrimethylammonium and Phenyltrimethylammonium. The adsorption of phenol on clay that was modified by Hexadecyltrimethylammonium was best described by Freundlich equation but Phenyltrimethylammonium modified clay adsorption was described by Langmuir equation. Adsorption of phenol towards Hexadecyltrimethylammonium modified clay is due to organic partitioning while adsorption on Phenyltrimethylammonium modified clays is a surface adsorption phenomenon. The adsorption efficiency of Hexadecyltrimethylammonium modified clays was depended on the organic carbon content and the orientation of the modifying agents whereas the adsorption efficiency of Phenyltrimethylammonium modified clay was depended on available surface area and the polarity of the surface (Richards and Bouazza 2007). Marsal. A *et al* investigated the adsorption of polyphenols on organo-bentonite from contaminated water. Polyphenols was obtained from vegetable extracts (mimosa) that was used in tanning processes of leather. Organo bentonite adsorption capability was effectively enhanced by increasing cationic surfactant ion concentration (Marsal, Bautista *et al.* 2009). Van Noi Nguyen *et al* used modified bentonite clay adsorbent that was synthesized by changing inorganic cations between layers of Thanh Hoa bentonite by organic cations like benzylhexadecyldimethylammonium, dimethyldioctadecylammonium and benzylstearyldimethylammonium. Addition of organic cations in the interlayer space of bentonite which increased the interlayer distance from 15 A˚ to 40 A˚. The adsorption capacity of organo-bentonite increased towards organic pollutants like Phenol, phenol red and DB 53 (Nguyen, Nguyen *et al.* 2013). Shen. Y used adsorption flocculation process in removing phenol by organo-bentonite from aqueous solution. In this process bentonite was dispersed in the phenol contaminated water and then adding cationic surfactant to increase its hydrophobicity. As a result agglomerates of organo-bentonite will form which bound phenol molecules from aqueous solution. These agglomerates will remove from water through sedimentation process. Through this process 90% phenol remove and approximately 100% organo-bentonite will recover (Shen 2002). Nourmoradi. H *et al* studied the adsorption of 4-chlorophenol on surfactant modified clay montmorillonite. Cation exchange capacity of clay was 150%, addition of surfactant ions on clay surface increased its adsorption capacity. Adsorption ability of hexadecyltrimethyl ammonium bromide montmorillonite was 29.96 mg/g and tetradecyl trimethyl ammonium bromide montmorillonite was 25.90 mg/g. Kinetics equilibrium data was followed kinetics pseudo-second order while adsorption isotherms was best described through Freundlich equation (Nourmoradi, Avazpour *et al.* 2016). Barreca. S *et al* used montmorillonite clay adsorbent and was modified by alginate beads,to enhanced its thermal and mechanicl stability. Na-alginate is a natural polymer and is extracted from sea weeds and used for decontamination of organic pollutants from water. Hybrid beads that contained alginate and montmorillonite are a best adsorbent for removing polychlorinated biphenyls PCBs from water (Barreca, Orecchio *et al.* 2014). Guanghai Xue *et al* provided a new type of modified clay adsorbent. Organically Montmorillonites were modified by two Gemini surfactants (1, 3 –bis (dodecyldimethylammonio)-propanedibromide and 1, 3 bis (dodecyldimethylammonio -2-hydroxypropane dichloride and is used for adsorbing of p-nitrophenol from aqueous environment. The maximum capacity at 25°C and pH 10 is 76.92 mg/g for BDP-Mt and 81.30 mg/g for BDHP-Mt. BDHP-Mt is more efficient adsorbent than BDP-Mt due to the presence of one hydroxyal group (Xue, Gao *et al.* 2013). Fatimah. I and Huda. T modify Indonesian montmorillonite for the adsorption of Toluene. Raw montmorillonite was modify to enhance its adsorption capacity by intercalation of surfactant ions like cetyltrimethylammonium (CTMA), which contributes an organophilic character in adsorbent. Adsorption not only enhanced by inserting surfactant ions in their interlayer spaces but also depends on CTMA concentration, CEC of montmorillonite clay and their CTMA/CEC ratio. The adsorption of Toluene on organo-clay revealed that it follow pseudo second order and Langmuir isotherms (Fatimah and Huda 2013). Arellano-Cárdenas *et al* used Porous Clay Heterostructure adsorbent and performed different experiments to show the adsorption of organic toxicant molecules like phenol and di-cholorophenol from aqueous solution (PCH). PCH have both hydrophobic and hydrophilic character due to the presence of silanol and siloxane groups formed during the pillaring and preparation of the PCH. So that's why porous clay Hetrostructure adsorbed both phenol and dichlorophenol from aqueous solution, otherwise it is very difficult to remove from water. The adsorption of di-chlorophenol described by Freundlich adsorption model while in case of phenol, Langmuir model was best to describe adsorption at high equilibrium concentration but at low equilibrium concentration Freundlich adsorption model was best to describe adsorption (Arellano-Cárdenas, Gallardo-Velázquez *et al.* 2005). Okada. T *et al* studied the adsorption of phenolic compound with the help of tris (2,2V-bipyridine) ruthenium (II)-clay from water. The adsorption capacity of phenolic compounds is a function of nature of clay. The interlayer spacing of modified-clay was not affected by adsorbed phenolic compounds. The adsorption of phenolic compounds on clay adsorbent strongly effected by means of the charge density in the interlayer spaces of clay. The adsorption of phenolic compounds on the tris (2,2Vbipyridine) ruthenium (II)-clays followed Langmuir type adsorption isotherms, and there is a strong interaction between them (Okada, Morita *et al.* 2005). Yuri Park *et al* synthesized and characterized an organo clay and used in removing p-nitrophenol from pollutant medium. In determining the sorption mechanism on organo-clays depends on concentration of surfactant. The importance of hydrophobic organoclays to remove organic pollutants from water (Park, Ayoko *et al.* 2011). K. O Martíneza *et al* studied selectively the adsorption of bisphenol and 2, 4-diclorophenol on the surface of composite clay material from their aqueous solution in single and multicomponent systems due to the presence of humic acid. Adsorption was studied in the presence of transition metals like nickel, copper and cobalt and it was found that the adsorption of organic pollutant increased with the inclusion of these metals on the unmodified clay in the presence of surfactant. The adsorbent was regenerated by thermal treatment/ washing with alkaline solution (Ortiz-Martínez, Reddy *et al.* 2016). Catrinescu, C *et al* used Fe-exchanged Al-pillared beidellite catalyst which was prepared by cation doping technique. Beidellite is 2:1 dioctahedral smectite clay. In the interlayer space of beidellite has a more ordered distribution of pillars that is why beidellite have higher thermal stability and a much stronger acidity. Fe-exchanged Al-pillared beidellite catalyst used wet peroxide for the oxidation of phenol (Catrinescu, Teodosiu *et al.* 2003). Wang. Y *et al* modified porous clay hetro-structure by incorporating template agent as a carbon source and then washed with H_2SO. Template agent changed the surface chemical properties, contained 5.35% carbon contents, 428 m^2/g large surface area and approximately 0.2 cm^3/g micropore volume. Porous clay hetro structure have greater adsorption capacity towards toluene (Wang, Su *et al.* 2016). Jia-Qian Jiang *et al* studied the behavior of modified clay (montmorillonites K10, KSF), adsorbent towards organic and inorganic contaminants. Montmorilinite can be improved by HDTMA surfactant, Al/Fe polymeric species as well as by using mixture of surfactant and polymeric species Fe/Al-HDTMA. Because of modification the surface area of clay become increase and hydrophobic. By introducing the modifier in the clay, they have the capacity to adsorbed both organic and inorganic contaminants (Jiang and Zeng 2003). Rytwo. G *et al* studied the adsorption of naphthalene and some phenolic compounds on clay that was modified by crystal violet or tetraphenylphosphonium ions on montmorillonite. Batch adsorption technique was used for this purpose (Rytwo, Kohavi *et al.* 2007). Senfeng Yang *et al* modify and characterized the surface and structure of clay montmorillonite to increase its adsorption capacity. For the first time Na-montmorillonite was modify by a novel aromatic-containing gemini surfactant, bis-N,N,N,-hexadecyldimethyl-p-phenylenediammonium dibromide (BHPD). The hydrophobicity of organo-clay was increased even at low concentration of (BHPD). The adsorption of 2-napthnol is greater than phenol under the same condition due to the stronger hydrophobicity of 2-naphthol and its higher delocalized p-electron density. The adsorption of 2-napthnol on organo-clay follow pseudo-second-order kinetics and have better agreement with Freundlich isotherm. The adsorption of 2-naphthol and phenol on organo-clay was spontaneous and endothermic process (Yang, Gao *et al.* 2015).

Adsorption of oil spills and petroleum hydrocarbons

All over the world environmental experts have been involved in development of processes and roles to prevent the discharge of pollutants into water. Many organic pollutants are released from oil and petrochemical industries,that have high polluting possibilities. These pollutants are considered as being stable towards light and heat and are also biologically un-degradable (Brandão, Souza *et al.* 2010). These pollutants decreases the contact area between water surface and atmospheric air, which block the passage of oxygen. Therefore researchers are interested to develop new materials, new methods and techniques for removal of pollutants and hazardous materials form waste streams before they are discharge into the environment. Petroleum hydrocarbons also cause vast changes in environment and effect water properties. Many methods were studied for removing of these types of pollutants. One of the most important technique was used to remove these pollutants is the adsorption process because they are low cost and easily handle (Namasivayam, Kumar *et al.* 2001, Amin 2008). A variety of materials have been modified and used as adsorbent material for oil and petrochemical pollutants (Lillo-Ródenas, Marco-Lozar *et al.* 2007, Gurgel, Júnior *et al.* 2008).

These materials are hydrophobic in nature with porous structure, have adsorption capacites towards oils and petrochemicals. Recently, clay constituents were studied and utilized as an adsorbent material for removing hydrocarbons effluents from water. Clay minerals are naturally abundant material with low cost and have large surface area (Qu, Zhu *et al.* 2009).

Onuma Carmody *et al* used organo-clays for the adsorption of oil spills from water. Organo-clay adsorbed oil spills because of high hydrocarbon sorption, retention capacities and hydrophobicity. Organo-clay was synthesized by modifying Wyoming Na-montmorillonite (SWy-2-MMT) with three surfactants.

(a) Octadecyltrimethylammonium bromide (ODTMA), formula $C_{21}H_{46}NBr$;

(b) Dodecyldimethylammonium bromide (DDDMA), formula $C_{22}H_{48}BrN$;

(c) di (hydrogenated tallow)dimethyl ammonium chloride (Carmody, Frost *et al.* 2007).

Maximum sorption of oil spills by clay is due to the presence of surfactant that contain two or more hydrocarbon long chains. El-Zahhar. A. A and Al-Hazmi. G. A used organically modified kalonite clay to adsorbed petroleum hydrocarbon. The adsorption of petroleum hydrocarbons on kalonite clay minerals was hindered by competing with water molecules relative to non-polar compounds on adsorbent material. Adsorption capacity of Kalonite, enhanced by replacing the inorganic cations with organic surfactant molecules like HDTMA. The adsorption capacity of clay was depended on contact time, HDTMA concentration and adsorbent dose also. Zhao, M *et al* explore the economically best and high performance exfoliated vermiculite (EV) adsorbent material. To enhance the adsorption capacity of exfoliated vermiculite, intercalated with carbon nanotube (CNT) contents. Sponge-like exfoliated vermiculite (EV)/carbon nanotube (CNT) hybrids will be formed. This adsorbent (EV/CNT) have a porous structure due to the presence of CNT contents. It was also floated on the surface of water due to its low bulk density. When the CNT content reached to 91.0% then the EV/CNT hybrids have highest adsorption capacity (26.7 g/g) for diesel oil. Their adsorption capacity for diesel oil can be further increased to 70.6g/g by transforming the EV/CNT hybrids into fluffy EV/CNT cotton through high-speed shearing (Zhao, Huang *et al.* 2011).

Adsorption of other organic pollutants

K. Ba *et al* performed batch experiment for the removal of $Cu^{2+,}$ Cl^{-}, and 2,4-dichlorophenoxyacetic acid from pollutant water on chitosan modified bentonite. Chitosan is used to modify the bentonite for improved its adsorption capacity. Chitosan contained a large numbers of –NH2 and –OH functional groups that provided the coordination sites for binding the pollutants on bentonite. The mass ratio of bentonite to chitosan was 1:0.01. Bentonite was prepared by three techniques: Na2CO3 treatment, thermal treatment and compound treatment and then was modified by chitosan which enhance its adsorption capacity. Because of their ability to resist unfavorable environment and fast growth rate (Ba, He *et al.* 2014). Xu. L *et al* used bentonite clay adsorbent for the removal of contaminants. To enhance its adsorption capacity towards aromatic hydrophobic pollutants naphthalene NA, bentonite was modified by aromatic long chain alkyl surfactant, cetyldimethylbenzylammonium. There was an electron-donar interaction and specific pi-pi interaction between the aromatic rings of CDMBA and NA was explored (Xu, Zhang *et al.* 2014). Chen. C *et al* studied the adsorbed and characterize Nitrosamines Nitrosodiphenylamine and its precursor Diphenylamine on modified bentonite clay from water. Batch test determines its kinetics, isotherm model and adsorption efficiency. Pseudo second order well described its kinetics equilibrium and adsorption isotherm was linear for Nitrosodiphenylamine which represents partitioning process occur between the adsorbate and modified clay. Whereas the nonlinear adsorption isotherm was Diphenylamine, and was well described by the Slips model which involved partition and electrostatic interaction in adsorption of precursor (Chen, Zhou *et al.* 2014). N. Jović-Jovičić *et al* partially modify the local bentonite by adding surfactant ions [hexadecyl trimethylammonium ions (HDTMA)] to organo-clay. Partially modify clay is an efficient adsorbent capable to simultaneously adsorb organic pollutants and as well as inorganic toxic metal cations. With increasing the HDTMA surfactant ions in the interlayer spaces of Bentonite clay adsorbent, the adsorption of Acid Orange 10 increases but adsorption of Pb^{+2}metal ions decreases. Its kinetic equilibrium data was successfully through pseudo second order (Jović-Jovičić, Milutinović-Nikolić *et al.* 2010). Wu. Z and Zhu. L removing organic pollutants from coking wastewater through adsorption by using organo-bentonite clay as an adsorbent material. Bentonite was modified by quaternary ammonium cationic surfactant molecules. Treatment of waste water with organo-bentonite is a simple and low cost procedure because it is a one-step process, both synthesis of clay and sorption of organic toxic pollutant from coking water done simultaneously (Wu and Zhu 2012). Oztekin. N *et al* studied the adsorption of polymer Polyethyleneimine on bentonite clay from water. There is an electrostatic interaction between the polyelectrolyte and the clay particles. This electrolyte effects on the properties of bentonite suspensions (Öztekin, Alemdar *et al.* 2002). Hongping He *et al* synthesized organo-montmorillonite which have wide applications in removing the organic pollutants from environment. Montmorillonite have different cation exchange capacity by surfactants with different chain length and chain number. The adsorption of organic pollutants strongly depends on the concentration of surfactant loadings, surfactant alkyl chain length and chain numbers. The loading of surfactant on clay minerals depends on CEC of montmorillonite (He, Ma *et al.* 2010). Qin Zhou *et al* examine the sorption of perfluorooctane sulfonate on organo-montmorillonite. The organo-montmorillonite are hydrophobic in nature because of the addition of cationic surfactant [hexadecyltrimethylammonium bromide (HDTMAB)]. The adsorption capacity of organo-montmorillonite increase by increasing the concentration of cationic surfactant. In sorption of PFOS on organo-montmorillonite involved two types of interaction occur between them i.e. hydrophobic interaction and electrostatic interaction but hydrophobic interaction played a dominate role in sorption of PFOS (Zhou, Deng *et al.* 2010). Zampori. L *et al* was investigated the adsorption of aromatic organic compounds, nitrobenzene and Orthochlorophenol on organo-montmorillonite adsorbent. Orthochlorophenol was strongly intercalated on the clay surface through hydrogen bonding and not easily desorbed as compared to Nitrobenzene. Greater extents of Nitrobenzene were adsorbed as compared to Orthochlorophenol because of the higher dipole moment (Zampori, Stampino *et al.* 2009). Pouya. E. S *et al* studied the adsorption of benzoic acid from water by organo-vermiculite in the presence of hydrophilic silicon dioxide nanoparticles by applying batch adsorption method. The equilibrium kinetics successfully defined by Temkin, Dubinin Radushkevich, Freundlich and Langmuir isotherms in the presence or absence of silicon dioxide nanoparticles. Nanoparticles enhanced the adsorption capacity of the clay towards benzoic acid. They used quadratic polynomial model for calculating the adsorbent capacity in the presence of nanoparticles was depended on adsorbate and nanoparticle concentrations. The adsorbent capacity of modified vermiculite was 36.83 mgm^{-1} when its initial concentration and nanoparticles was 969.2 mgL $^{-1}$, (Pouya, Abolghasemi *et al.* 2016). Bée. A *et al* used multi-functional adsorbent for the elimination of both cationic and anionic contaminants distinctly or together. The adsorbent was prepared by encapsulating magnetic nanoparticles and clay in cross-linked chitosan beads. The magnetic material that was used is a Ferro-fluid containing magnetic nanoparticles of maghemite having surface charges and easily recover them at the end of the adsorption process. The clay that was encapsulated in the beads allows observing *the* selectivity of adsorption (Bée, Obeid *et al.* 2017). Nkansah.M.A, *et al* explored light weight expanded clay aggregate (LECA) for the removal of Polyaromatic hydrocarbons (phenanthrene, fluoranthene and pyrene) from waste water. The sorption of PAH on LECA strongly depends on contact time sorbent concentration. Greater the amount of LECA then greater will be the removal of PAH. The capacity of sorbent also influenced by the hydrophobicity of PAHs. The sorption of the PAHs followed the order PYR > FLU> PHE, which depends on the PAH- hydrophobicity (Nkansah, Christy *et al.* 2012). P. Ferreira *et al* synthesized the new porous benzene-silica hybrid clay heterostructure which is used in the adsorption of volatile organic compounds. HPCH can be prepared by template-method. The porous benzene-silica hybrid clay hetrostructure have large surface area due to porous structure. Due to high hydrophobicity and thermal stability, it has a wide applications in removing the volatile organic compounds from waste water (Ferreira, Nunes *et al.* 2006). Fang Qu *et al* demonstrate the adsorptions of volatile organic compounds (VOCs) on porous clay heterostructures (PCH).We investigate the six VOCs like acetone, toluene, ethyl benzene, o-xylene, m-xylene and p-xylene that are adsorbed on porous clay hetrostructure. The adsorption capabilities of VOCs were intensely depend on cross-sectional area, enthalpy of vaporization, polarizability and critical volume. Due to the HOMO energy values of VOCs, PCH have more adsorption affinity for acetone than that for aromatic compounds (Qu, Zhu *et al.* 2009).

Conclusion

In this review, a variety of clay adsorbents and organic pollutants have been discussed. Low cost, effective and locally available clay material could be utilized for removal of organic pollutants (dyes, herbicides, fungicides, pesticides, pharmaceutical products, oil spills and other organic aromatic phenolic compounds) from aqueous medium instead of using expensive commercial activated carbon. Absolutely, clay adsorbents comprise a promising benefits for removing organic pollutants commercially in future. Also demonstrated the modification of clay adsorbent to enhance its adsorption properties toward organic pollutants. Surface area of clay adsorbents increase by modifying its surface area by using organic compounds and different types of surfactants.

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