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Removal of Effluent from Petrochemical Wastewater by Adsorption Using Organoclay

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1. Introduction

Given that environmental policy is increasingly severe, the industries are constantly seeking to establish standards of ever lower concentrations of the pollutants in wastewater, and are gradually adjusting their processes, with new procedures in order to generate less and remove more toxic elements present in their discharges.

The production stages of a petroleum industry, such as extraction and refining, are potentially responsible for generating large volumes of effluent to be discarded in the environment.

Water contaminated with petroleum derivates is produced in large volumes in many stages of refining oil. This mixture should be treated to separate these derivates from water before it can return to the environment. However, treatment with conventional processes is very often not economically feasible, or do not have the appropriate efficiency with regard to separation, or produce large amounts of mud that also need treatment (Almeida Neto et al., 2006).

The waste generated in oil refineries contains many different chemical compositions, depending on the complexity of the refinery, the existing processes and the type of oil used. The effluents are produced mainly by physical separation processes, such as atmospheric distillation and vacuum distillation, deparaffinization, deasphalting and also by processes involving chemical conversions by isomerization, alkylation, etherification, catalytic reform, etc.

The risks of environmental contamination and to human health caused by volatile organic compounds have driven a lot of research designed to eliminate or remedy its deleterious effects. Several of these compounds, such as phenol and BTEX compounds (benzene, toluene, ethyl benzene and the isomers of xylene) are found in effluents from oil refineries, and they are important contaminants due to their high toxicity (Akhtar, 2007).
Volatile organic compounds (VOCs) are usually harmful and carcinogenic and may cause serious environmental problems which affect ecosystems. The VOCs also may cause adverse effects to human health, even in low concentrations (Benmaamar & Bengueddach, 2007). They are known to integrate a group of compounds that most contribute to the formation of photochemical ozone and secondary organic aerosols (SOAs), increasing to global warming (Hu et al., 2008).

Different technologies such as advanced oxidation, biofiltration, separation by membrane, absorption and adsorption have been studied and developed in order to remove these organic compounds. It happens that many of these procedures, due to high operating costs, become unviable.

The phenols appear in the effluents from an oil refinery in the stages of catalytic cracking, production of lubricants and solvents, and in the rinse water of the gasoline. According to a survey, the average concentration of phenol in the effluents was 154 mg L\(^{-1}\) (Mariano, 2001). Another study found that the concentrations of phenolic effluents from a refinery were between 0.9 mg L\(^{-1}\) and 60.0 mg L\(^{-1}\) (Barros Junior, 2004).

Among the organic pollutants present in effluents from oil refineries at higher concentrations, phenol stands out. The phenol is a pollutant that is generated mainly in catalytic cracking and fractioning of crude oil. In addition to these sources, some processes use phenol as a solvent, increasing your concentration in the effluent (Otokunefor & Obiukwu, 2005). This study, based in Nigeria, evaluated the impact caused by the release of effluents from a refinery into a body of water. This study found that the quantity of phenol in the effluent treated released in the river delta showed a level of 1.84 mg L\(^{-1}\), higher than the maximum allowed under Nigerian law which sets it at 0.5 mg L\(^{-1}\). The phenol is one of the most difficult wastes to be removed, usually involving processes that are far from satisfactory and have high operating costs. Moreover, it is a highly toxic substance that can kills fish and other aquatic organisms.

The presence of hydroxyl groups confers to phenols the ability to form hydrogen bonds, which gives the same boiling points above organic compounds of molecular weights close, in addition to presenting high solubility in water. The phenol has solubility 8.3 g per 100 g of water at 25°C, therefore, the phenol may go dissolved in the aqueous industrial waste (Solomons & Fryhle, 2002).

The BTEX compounds are considered organic pollutants with high toxicity. One research found that among organic pollutants common in industrial accidents, leaking storage tanks or organic effluents, the BTEX compounds are present at high frequency, being directly responsible for contamination of waters and soils. These aromatics are extremely harmful to human health, fauna and flora (Sharmasarkar et al., 2000).

Liquid wastes generated by refineries have different chemical compositions including oil and grease, phenols, BTEX, ammonia, suspended solids, cyanide, sulfide, nitrogen compounds and heavy metals such as iron, cadmium, nickel, chromium, copper, molybdenum, selenium, vanadium and zinc. Seeking to evaluate and monitor the environmental impact caused by the discharge of effluents in water bodies, toxicity tests are often used as indicators of damage to the aquatic environment. Tests on fish, invertebrates and seaweeds have revealed that most of
effluents from refineries is toxic, causing in these organisms not only lethal effects as well as changes to their growth and reproduction (Wake, 2004).

Many hydrocarbons, particularly the aromatics, have certain solubility in water, such as benzene, 1800 PPMV, toluene, 470 PPMV, ethyl benzene, 150 PPMV and xylenes, 150 PPMV. The process of desalter was very relevant to the contamination of BTEX in aqueous effluents at refineries studied (Worrall & Zuber, 1998).

Experiments have shown that different formulations of gasoline may affect the fate and transport of BTEX compounds. The use of ethanol as an ingredient in the formulation of gasoline has increased worldwide, in order to minimize atmospheric pollution resulting from combustion. The ethanol is completely miscible with water. The ethanol increases the solubility of BTEX compounds in water due to the effect of co-solvent. The International Agency for Research on Cancer (France) and the National Institute for Occupational Safety and Health (USA) include benzene in their lists of products carcinogens. Among the cancers, leukemia is the most frequent. In Brazil, the carcinogenic action of benzene was officially recognized as of March 1994. Your capacity to cause chromosomal damage and to bone marrow was widely demonstrated in humans and animals (Tiburtius & Zamora, 2004).

By understanding the development compatible with the preservation of natural resources, new techniques for wastewater treatment are needed. The clays have a high technical economic feasibility due to the adsorption potential, which associated with its abundant availability make the material more accessible adsorbents (Rodrigues et al., 2004).

The adsorption using clay constitutes one of the techniques recently applicable for the treatment of contaminated effluents. The material is abundant, has low cost and has large surface area. Moreover, it has high rates of mass transfer (Qu et al., 2009).

The increasing use of compounds and products originating in oil has caused serious problems to human health and the environment. The hydrophilic montmorillonite clay is an ineffective adsorbent for aromatic compounds that move often from contaminated sites. The effect of adsorption is suppressed by the competition of water in relation to non-polar compounds to the surface of the adsorbent material. The adsorption of organic compounds on montmorillonite can be enhanced by replacing the inorganic cations presents in the original structure to surfactant cations, such as: hexa-decile-trimethyl-ammonium, HDTMA, tetra-methyl-ammonium (TMA), tetra-ethyl-ammonium (TEA), tetra-butyl- ammonium (TBA), and tri-benzyl-methyl-ammonium (TBMA). Adsorbents surfactants slow the migration of pollutants in subsurface becoming an effective barrier transport of these (Yasser & Jamal, 2004).

Physical and chemical modifications of clays have been used for the production of materials for practical applications. The properties of clay can also be modified by adsorption and intercalation of organic polymers. The pillarization is a modification method that usually involves the intercalation of cationic species acting as pillars to support the mineral layers, separating them, creating a porous material useful for adsorption of organic compounds and other environmental applications (Bergaya et al., 2006).

The pillared clays (PILCs) are microporous materials obtained by intercalation of inorganic species in natural or synthetic expandable clays. Currently the PILCs are considered promising
materials in various processes of adsorption and catalysis, and in particular in processes that relate to environmental protection. They result from isomorphic substitution of aluminum and silicon atoms by atoms of lower valence. Their applications can be found in the removal of NO\textsubscript{x}, adsorption of toxic organic compounds, among others (Pires et al., 2000).

The process of pillarization consists in intercalation of cationic complexes, followed by calcination. Inorganic complexes can be obtained by hydrolysis of the metals of group 13 and transition metals, by changing the clay basal spacing of 1.2 nm to 1.8 nm, or more (Leite et al., 2000).

The abundance of world reserves of bentonite makes it impossible to estimate the quantity of these resources in a global context. In Brazil the estimated reserves are approximately 47 million tonnes, of which 47.7% are in the State of Paraná, in the municipality of Quatro Barras, 26.6% are in the State of São Paulo, in the municipalities of Taubaté and Tremembé and 25.3% are in the State of Paraíba, in the municipalities of Campina Grande and Boa Vista. The main consumers of these materials are petroleum companies, to employ the clay as thixotropic agent for use in drilling wells, industries that work with iron ore pellets for use as binding agent, paint and varnish industries, among others (Oliveira, 2004).

2. Fundamentals of adsorptive processes

The phenomenon of adsorption is known since the eighteenth century, when it was observed that a certain kind of coal had retained in their pores large amount of water vapor. Nowadays, the adsorption processes are applied in the purification and separation of substances, presenting itself as an important alternative and economically viable in many cases (Fogler, 2002; Ruthven, 1984).

Adsorption phenomena are classified in two types: physical adsorption and chemical adsorption. In the chemical adsorption exists an effective exchange of electrons between the solid and the adsorbed molecule, causing the following: formation of a single layer on the solid surface, irreversibility, and great force of attraction between the adsorbent and adsorbate. For this reason this type of adsorption is favored by increased temperature and pressure. The physical adsorption is a reversible phenomenon, where usually observed the deposition of more than one layer of adsorbate on the adsorbent surface. The forces acting on the physical adsorption are the Van Der Waals forces. The energy released is relatively low and rapidly reaches equilibrium. In this process, the temperature increase is detrimental to the adsorption efficiency.

The adsorption separation processes are widely used in industry, particularly in oil refineries and petrochemical industries (Ruthven, 1984). Knowledge of physical and chemical principles in which they are inserted adsorptive processes is fundamental to the interpretation of adsorption phenomena. The kinetic aspects and the adsorption equilibrium form the theoretical basis for understanding between the fundamental principles and industrial practices. These parameters are therefore essential to the analysis and interpretation of experimental data serving as a support for the dynamic study of the adsorption columns.

Research involving adsorptive processes between organoclay and organic compounds found their interpretations of experimental data supported according to the Langmuir's model,
which assumes the existence of adsorption sites, all energetically equivalent, where only one molecule is adsorbed per site, without any interaction with molecules adsorbed on neighboring sites (Burns et al., 2003; Lin et al., 2005). However, there are studies that point to other adsorptive representative models such as Freundlich’s model that considers non-uniformity in terms of surface adsorption site (Boufatit et al., 2007; Cavalcanti et al., 2009; Irene et al., 1998; Kessaïssia et al., 2004; Ko et al., 2007; Richards & Bouazza, 2007; Sameer et al., 2003; Viraraghavan & Alfaro, 1998). Other studies have used the model of Dubinin-Raduskevich, which represents a more comprehensive model. In this model the surface of the adsorbent is not homogeneous and the interaction energy is not constant (Akçay, 2004, 2005).

2.1 Langmuir’s isotherm

The kinetic of adsorption starts from the net adsorption rate \( r_A \) (mg g\(^{-1}\) min\(^{-1}\)), represented by Equation 1.

\[
r_A = \frac{dq_A}{dt} = k_{AD}C_A(1 - \theta_A) - k_D\theta_A
\] (1)

Being \( C_A \) the concentration of the adsorbate in the liquid phase (mg L\(^{-1}\)), \( k_{AD} \) the kinetic constant of adsorption, \( k_D \) the kinetic constant of desorption and \( \theta_A \) the fraction of adsorption sites occupied by component A of the total number of sites occupied at saturation.

At equilibrium, the net rate of adsorption is null, so we can rewrite Equation 1 according to Equation 2.

\[
k_{AD}C_A(1 - \theta_A) = k_D\theta_A
\] (2)

By introducing the constant of equilibrium \( K_A \), which represents the ratio between the kinetic constants of adsorption and desorption, in Equation 2, we have Equation 3.

\[
K_A = \frac{k_{AD}}{k_D}\frac{\theta_A}{C_A(1 - \theta_A)}
\] (3)

Reorganizing the terms and rewriting Equation 3 as a function of the fraction of sites occupied \( \theta_A \) we obtain Equation 4.

\[
\theta_A = \frac{K_AC_A}{1 + K_AC_A}
\] (4)

Considering the fraction of sites occupied \( \theta_A \) as the ratio of the concentration of the adsorbate on the solid phase \( q_A \) (mg g\(^{-1}\)) and the concentration of adsorbate in solid phase in saturation \( q_{max} \) (mg g\(^{-1}\)) also known as maximum adsorption capacity, we have Equations 5 and 6, the latter being known as the Langmuir’s Equation.

\[
\theta_A = \frac{q_A}{q_{max}}
\] (5)
The Langmuir’s equation can be linearized, yielding experimental values of the equilibrium constant $K_A$ and maximum adsorption capacity $q_{max}$, according to Equation 8.

$$\frac{q_A}{q_{max}} = \frac{K_A C_A}{1 + K_A C_A}$$

The Langmuir’s isotherm is one of the most common models used to represent equilibrium behavior in the adsorption process. Its main concept proposes the uniformity in terms of surface adsorption sites with adsorption monolayers. Also considered independent interactions of neighboring sites and possibilities of dynamic equilibrium of adsorption and desorption (Fogler, 2002; Ruthven, 1984).

### 2.2 Freundlich’s isotherm

It is an equilibrium model for indicating a greater degree of generalization of the adsorptive process. Now, it is considered the non-uniformity in terms of surface sites and multilayer adsorption (Ruthven, 1984). Its general expression for a single component system is represented by Equation 9, known as the Freundlich’s Equation.

$$q = K C^{1/n}$$

The Equation 9 assumes a linear form as shown in Equation 10.

$$\ln q = \ln K + \frac{1}{n} \ln C$$

The parameters of Equation 10 will be obtained experimentally. Being $K$ the equilibrium constant feature of the Freundlich’s isotherm and $1/n$ adsorption intensity.

### 2.3 Dubinin-Raduskevich’s isotherm

Another adsorptive equilibrium model was also used in adsorption of phenol and BTEX in organoclay. This is the Dubinin-Raduskevich’s model, represented by Equation 11 (Akçay, 2004, 2005).

$$\frac{q}{q_{max}} = \exp(-\beta e^2)$$
constant. Being \( q \) the concentration of the adsorbate on the solid phase (mg g\(^{-1}\)), \( \beta \) the constant related to adsorption energy (mol\(^2\) kJ\(^{-2}\)), \( q_{\text{max}} \) the maximum adsorption capacity and \( \varepsilon \) the Polanyi potential, calculated according to Equation 12.

\[
\varepsilon = -RT \exp \left( \frac{1}{C_A \ v_{eq}} \right)
\]  
(12)

2.4 Kinetic models adsorptive

Some adsorptive kinetic models were used in different works of adsorption of organic compounds in organophilic clays, including models of Lagergren, also called models of pseudo-first order and pseudo-second order, represented by Equations 13 and 14 (Akçay, 2004, 2005; Cavalcanti et al., 2008; Yilmaz & Yapar, 2004).

\[
\frac{dQ}{dt} = k_{1\text{ads}}(Q - Q_{eq})
\]  
(13)

\[
\frac{dQ}{dt} = k_{2\text{ads}}(Q - Q_{eq})^2
\]  
(14)

Which \( Q_{eq} \) represents the equilibrium concentration in solid phase and \( Q \) the concentration in the solid phase over time, \( k_{1\text{ads}} \) (min\(^{-1}\)) and \( k_{2\text{ads}} \) (g mg\(^{-1}\) min\(^{-1}\)) the kinetic constants adsorptive related to models of pseudo-first order and pseudo-second order.

The analytical solution of Equations 13 and 14 are described by Equations 15 and 16 respectively.

\[
\ln(Q - Q_{eq}) = \ln Q_{eq} - k_{1\text{ads}}t
\]  
(15)

\[
\frac{t}{Q} = \frac{1}{k_{2\text{ads}}Q_{eq}^2} + \left( \frac{1}{Q_{eq}} \right) t
\]  
(16)

According to the model represented by Equation 15, we can determine the kinetic constant of first-order \( k_{1\text{ads}} \) through the slope of the straight line plotted between \( \ln (Q - Q_{eq}) \) versus \( t \), and we can determine the kinetic constant of second-order \( k_{2\text{ads}} \) through the interception of Equation 16.

3. Utilization of organophilic smectite clays as adsorbents of phenol and BTEX compounds

Below, we highlight the study of the smectites clays, the main procedures to make them organophilic and its application as an adsorbent for phenol and BTEX.

3.1 General structure of smectite clays and their properties

The classic definition refers to clay as a natural material, earthy, fine-grained that when moistened with water features plasticity (Souza Santos, 2002). The clay minerals are hydrated silicates that have layered structure composed of solid sheets formed by
tetrahedral of silicon (or aluminum) and oxygen, and leaves formed by octahedral of aluminum (magnesium, iron), oxygen and hydroxyls. One way of classifying clays is related to the type of cation present in the octahedral sheet. If that is divalent cation (such as Ca$^{2+}$ or Mg$^{2+}$) all octahedral are occupied and the clay would be classified as type tri-octahedral. For trivalent ions (such as Al$^{3+}$), only 2/3 of the sites will be busy, so it is denominated as bi-octahedral type clays. The nomenclature for the types of layers is a simple expression of the ratio between the tetrahedral sheets and octahedral sheets. Therefore, a 1:1 layer clay mineral has a tetrahedral and octahedral sheet, while a 2:1 clay mineral type has two tetrahedral sheets and one internal octahedral. The distance $d_{001}$ is called interlayer distance and is also used to classify the different clays exist (Neumann et al., 2000).

The clay minerals are formed mainly of hydrated silicates of aluminum, iron and magnesium, containing certain amount of alkaline and alkaline earth elements (Rianelli & Pereira, 2001). Clays are minerals that have unique physical and chemical characteristics. They are formed by small crystals, usually in the form of hexagonal platelets, which agglutinates to form conglomerates. These platelets are composed of aluminosilicates organized, composed of the elements silicon, aluminum and oxygen, and others in smaller proportions, such as magnesium and iron. When hydrated, allows the separation of lamellar layers and intercalation of ions and molecules. The understanding of the properties of organized systems leads to interest in the study of systems consisting of the structured clays (Pastre et al., 2003). For being generally of sedimentary origin, the clay can contain a large number of other minerals, represented by grains of varying diameters, soluble salts and organic matter.

The clay minerals are subdivided into crystalline silicates with layer lattices or lamellar, and crystalline silicates with fibrous lattice structure, chain lattices. The silicates of lamellar structure can be divided into three groups or families: dimorphic (layer 1:1), trimorphic (layers 2:1) and tetramorphic (layers 2:2). The nomenclature 1:1 and 2:2 refers to the number of layers of SiO$_4$ tetrahedral and octahedral of hydroxides, respectively, entering the establishment of the unit cell of the crystalline lattice of clay minerals.

**Exchangeable Cations, Oxygen, Hydroxyl, Silicon, Aluminum**

Fig. 1. Schematic representation of the crystal structure of smectite.
The paligorsquita or attapulgite and sepiolite are the only representatives of the fibrous structure of silicates.

The basal interplanar distance, the degree of substitution in the octahedral layer of the unit cell and the possibility of the basal layers to expand with the introduction of polar molecules are structural properties that allow the subdivision of lamellar structure of clay minerals.

The group of smectite clay minerals (montmorillonite, beidelita, nontronite, volcanscoita, saponite, sauconita, hectorita) is composed of two silicate tetrahedral sheets with a central octahedral sheet, joined by common oxygen atoms to the leaves, as shown in Figure 1. The leaves are continuous in the directions of crystallographic axes.

Sodium is the predominant exchangeable cation to increase the interlayer of smectite. The increase occurs by adsorption of water molecules by sodium, as shown in Figure 2.

![Fig. 2. Polycation not hydrated smectite clays and hydrated with sodium.](image)

The clay treated with quaternary salts develops the ability to swell by adsorption of organic molecules, resulting in the organoclay, as shown in Figure 3.

![Fig. 3. Development of organoclay treated with quaternary salt (Martins, 2007).](image)
Sodium clays can be used as adsorbents of inorganic compounds, and also as a thixotropic agent for drilling of wells water-based. Organoclay can be used as adsorbents of organic compounds, and also as a thixotropic agent for drilling of wells oil-based. The thixotropic property of gels is extremely important in drilling for oil exploration because they promote increased service life of the drill, torque reduction, increased stability and temperature control in the well. In a general way, any outages in wells, the rocky debris produced by the action of the drill are kept in suspension in the fluid, preventing the loss of the pit of debris by sedimentation and subsequent burial of partial probing tools, as shown in Figure 4.

Fig. 4. Oil well drilling - real situation (a) and hypothetical situation (b).

The group of kaolinite is formed by regular stacking 1:1, where each layer consists of a sheet of SiO$_4$ tetrahedra and a sheet of octahedra Al$_2$O(OH)$_6$ linked together in a single layer through common oxygen.

Replacements of ions Si$^{4+}$ leaves tetrahedral by ions of Al$^{3+}$, or Al$^{3+}$ by Mg$^{2+}$ or Ca$^{2+}$ in the leaves octahedral, are called substitutions isomorphic, and do not cause distortion in the structure of the lamellae, being all these atoms of similar size. In contrast, these substitutions generate an excess of negative charge in the layers of clay, which is responsible for some of the interesting properties of them. The excess negative charge is compensated by the adsorption of cations on the external surfaces of the layers, where the amount of adsorbed cations required to neutralize the negative charges in the layers of the material is measured by the cationic exchange capacity (CEC). This property is also related to the extent of isomorphic substitution. The CEC of the montmorillonite clays is between 40 and 150 meq (or mmol currently) per 100 g of clay (Gomes, 1988).

Clays are widely used as adsorbents due to its large surface area. On the other hand, its adsorption capacity for organic molecules, water soluble is very low. This is due to the hydrophilic nature of mineral surfaces. Treatment of clays with organic and inorganic reagents increases its adsorption capacity. The modified clays can be used as adsorbents in treatment systems of wastewater, thus preventing contamination of groundwater. The
potential of organically modified clays as adsorbents for organic contaminants effective in preventing and reducing pollution has stimulated studies on their adsorptive properties. The adsorption of organic compounds in organoclay occurs through several mechanisms, such as ionic reactions and complexation (Vieira et al., 2004).

The natural smectite clays, whose cation for exchange is sodium, produce gels that can be used as thixotropic agents in drilling fluids for oil wells based on water. Due to the hydrophilic environment on the surface, natural smectite is not an effective sorbent for nonionic organic compounds in water even if the clay has a high specific surface area. Reactions of ion exchange may greatly modify the surface properties of natural smectite. When, for example, organic cations of formula \((\text{CH}_3)_3\text{NR}^+\), where \(R\) is an alkyl hydrocarbon, occupy the local exchange of smectite, the surface properties transforms from hydrophilic to hydrophobic (Chiou et al., 1983). Once such organic cations are fixed on the surface of smectite, an organic phase is formed which is derived from the alkyl hydrocarbon. This effectively removes the nonionic organic compounds from water with hydrophobic interactions.

The modified clays are normally prepared using a quaternary ammonium cation of general formula: \([(\text{CH}_3)_3\text{NR}]^+\) or \([(\text{CH}_3)_2\text{NRR'}]^+\) where \(R\) and \(R'\) are hydrocarbons. The adsorptive properties of clays depend on the molecular size of the groups \(R\) and \(R'\) (Bodocsi et al., 1997). When the sizes \(R\) and \(R'\) are small, such as: -\(\text{CH}_3\) and phenyl, such clays are classified as adsorbents. When \(R\) or \(R'\) are long-chain, these clays are classified as organophilic clays. Many studies indicate that polar organic compounds such as alcohols, amines and ketones were adsorbed on the clay interlayer spaces, and probably at the edges of clay particles by electrostatic attractions and by ion exchange reactions. Herbicides and insecticides can be also adsorbed by organophilic clays and become inactive.

One research revealed that treatment of smectite clays with quaternary ammonium salts in concentrations higher than their CEC corroborates with the increase in adsorptive capacity due to the setting of quaternary ammonium ions in the interlayer regions and in the external surface of clay minerals, with the possibility of their interlayer regions exceeds 4.0 nm, resulting in delamination of the clay (Menezes et al., 2007).

Researchs confirm the possibility of development of smectite clays in adsorptive properties of the sedimentary watershed of the Araripe-PE, from the establishment of optimal experimental conditions grounded in factorial planning and response surface analysis, as tools of optimization of the process of activation of the clays. These studies proved the existance of calcic smectite clays with potential to develop organophilic properties, present in the sedimentary watershed of various municipalities in the Northeast. These clays have naturally polycations, with a predominance of magnesium and calcium, which, after exchange for sodium, develops thixotropy (Baraúna, 2000). The results of tests conducted on clays of the region showed that: a) these clays are composed of groups of clay minerals smectite and kaolinite; b) the mineral assemblage consists essentially of the smectite group; c) the predominants exchangeable cations are calcium and magnesium; d) clays treated with sodium develops thixotropy, with your plastic viscosity in aqueous suspensions with a concentration equal to 4.86% by mass equal to 3.0 mPas. This result is close to that recommended by Petrobras which recommends, among other analysis, minimum plastic viscosity equal to 4.0 mPas (Petrobras, 1997a, 1997b, 1998a, 1998b).
Another academic work was consisted in the preparation of an organophilic adsorbent material, starting from five different types of clays taken from watershed located in the Northeast of Brazil, as follows: “Verde Lodo”, “Bofe” and “Chocolate” taken from the municipality of Campina Grande, State of Paraíba; “Lagoa de Dentro” e “São Jorge”, taken from the Plaster Pole of Araripe, Pernambuco’s State. The fresh clay were treated with a solution of sodium carbonate in order to exchange the existing polycations in their interlayer regions by sodium in a batch reactor with different concentrations of this cation, contact time and temperature, according experimental design with a 23. As an answer to treatment with sodium carbonate, it was the reading of the viscosities of aqueous suspensions of plastic material with 4.86% by mass. The results showed that the clay Chocolate treated with sodium, in the best condition of the experimental planning, got a plastic viscosity equal to 4 mPas, according to the methodology described in Petrobras 1998a and Petrobras 1998b.

Then, there was a treatment with quaternary ammonium salt (chloride hexa-decile-tri-methyl-ammonium), and measured up to its apparent viscosity for dispersions in an oily medium containing 336 mL of 5391 Ultra-lub ester of Oxiteno and 84 mL of saturated solution of sodium chloride, with 2.4 g, 6.0 g, 9.6 g and 13.2 g of organoclay, resulting in 8.5, 10.0, 12.5 and 16.0 mPas, respectively, according to the methodology described in Petrobras 1997a and Petrobras 1997b. These results suggested that sodium clay and organoclay could be indicated as thixotropic fluids for drilling wells. Then, a study was conducted for adsorptive removal of phenol in synthetic wastewater using this organoclay produced. The results indicated a more than 80% removal of organic contaminants (Cavalcanti et al., 2009; Cavalcanti et al., 2010; Portela et al., 2008).

### 3.2 Adsorption of phenols and BTEX onto organoclays

Several physicochemical methods and biological have been used to remove organic compounds in industrial effluents. Application of membrane filtration systems and adsorption processes in water treatment and effluent was used by a group of researchers. They developed a system for removal of phenol from an aqueous solution through a combined process of ultrafiltration and adsorption using kaolinite and montmorillonite. The adsorption experiments were performed in batch with 0.2 g of clay and 100 mL of water contaminated in the range of variable concentration of the organic compound from 20 to 1000 mg L\(^{-1}\), stirred for 12 h at 25°C. The results showed that the phenol removal efficiency was 80% and a maximum adsorption capacity equal to 40 mg g\(^{-1}\) (Lin et al., 2005).

Other survey was developed to increase the range of applicability of the clays in the treatment of organic waste present in wastewater. The retention properties by adsorption of volatile organic compounds such as phenol, chlorobenzene and orthoxylene by a geomaterial composed of bentonite, activated carbon, cement and a water-soluble polymer in different operating conditions were evaluated. The operation was performed in batch at 25°C, using phenol, orthoxylene and chlorobenzene, without further treatment. The solutions were prepared in concentrations ranging from 50 to 400 mg L\(^{-1}\) with 0.3 g of the adsorbent material in 50 mL of solution distributed in erlenmeyer flasks. After the equilibrium established, the contaminated samples were centrifuged for 20 min at 2000 rpm. The kinetic results obtained for adsorption of these compounds in geomaterial, an initial concentration of 100 mg L\(^{-1}\) indicated residual concentrations of orthoxylene, chlorobenzene and phenol, respectively 40, 30 and 20 mg L\(^{-1}\) for a balance established in 12 h (Kessaïssia et al., 2004).
Two researches studied the adsorptive properties of montmorillonite clay modified by tetra-butyl ammonium (Akçay, 2004, 2005). The adsorption of p-chlorophenol in this clay was done in batch with 20 mL of pollutant solution to 0.1 g of clay, at 25°C for 16 h. The adsorption isotherms were adjusted according to the models of Freundlich and Dubinin-Radushkevich. The kinetic and thermodynamic parameters pointed to the application of organoclay as adsorbent effective of phenolic compounds in contaminated effluents.

Essays observed the adsorption, in batch, of phenolic compounds such as phenol and the isomers 2, 3 and 4-chlorophenol in smectite clays treated with chloride of tetra-methyl ammonium (TMA) and bromide of tetra-methyl-phosphonium (TMP). The experiments were performed with 100 mg of clay in solutions of adsorbate equal to 0.02 to 0.15 (mmol/100mL) in erlenmeyer of 250 mL, at 20°C. It was found that the smectite clay treated with TMP was better than the same adsorbent treated with TMA (Lawrence et al., 1998).

Other research confirmed the influence of the modification of bentonite in their adsorptive properties. The adsorption isotherms were determined with solutions of phenol in concentrations 50 mg L⁻¹ to 1000 mg L⁻¹, in pH 6.5, at 20°C and 24 h. Structural changes were carried out with tetra-decyl-trimethyl-ammonium bromide (TDTAB) and hexa-decyl-trimethyl-ammonium bromide (HDTAB), with changes in 25%, 50% and 100% of capacity exchange cation. The equilibrium time was approximately 7 h and kinetic results indicated the possible presence of heterogeneous regions on the surfaces of clays modified with 25% and 50% of its cation exchange capacity. The clays modified with TDTAB and HDTAB in 100% obtained the best results for the removal efficiencies (Yilmaz & Yapar, 2004).

Studies evaluating the adsorptive efficiency in modified bentonite to remove aromatic compounds (BTEX) present in aqueous solutions were performed. The results showed that the agent "dimethyl di-hydrogenated" increased the basal spacing of bentonite in 119%. The study demonstrated that the removal efficiency by adsorption to the compounds, benzene, toluene, ethyl benzene and o-xylene was 75%, 87%, 89.5% and 88.5%, respectively (Bodocsi et al., 1997).

In another study were investigated the effects of phenol in adsorptive organoclay with different characteristics. The adsorption experiments were performed in batch with 0.2 g of modified clay with 22 mL of phenol solution at pH 7 for 4 h. The equilibrium time, in preliminary studies pointed 2 h. The results showed the influence of modified clays in adsorptive power. According to the author, a change in the smectite interlayers increased the effectiveness of interactions between the phenol and the organoclay. Therefore, this clay is an effective adsorbent material for removal of nonionic organic compounds (Shen, 2005).

The organoclay dicetyldimethylammonium-bentonite was studied for adsorption of the compounds BTEX (nonionics and nonpolar) and of the compounds 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol (ionizable and polars). An experiment showed this preference in the adsorptive efficiency order: benzene < toluene < ethyl benzene < ortho-xylene; phenol < 2-chlorophenol < 2,4-dichlorophenol < 2,4,6-trichlorophenol (Irene et al., 2006).
3.3 Factors that can influence the process adsorptive

Some authors investigated physical factors that can interfere with the adsorptive process, such as pH and temperature, interfering on the steady state (Cavalcanti et al., 2009; Irene et al., 1998; Lin et al., 2005; Vianna et al., 2001).

3.3.1 Influence of pH

The rejection of the removal of phenol and o-cresol was related to the increase in pH of the system. For phenol, the rejection at the kaolinite was at pH 8.2, while for montmorillonite at pH 9.1. For o-cresol, the maximum rejection at the kaolinite was at pH 9.2, while for montmorillonite at pH 10.2. This result can be explained by the difference between the pKa of the phenolic compounds and the zeta potential of clays (Lin et al., 2005).

Studying the influence of pH on the adsorptive process, it was observed that changing the pH (5, 7, 9) was not as relevant for changes in the adsorption isotherms of BTEX compounds in "DCDMA-bentonite" (dicetyldimethylamonium-bentonite). The result observed is not due to dependence on pH with the adsorptive process, but the forces of attraction between molecules of BTEX and sites of modified clay. For phenol, this research group concluded that the change of pH (5, 7, 9), leads to a slight change in the adsorption isotherms. The increase in pH decreases the affinity of the clay used with phenol. This is due to the fact that the lower the pH in relation to the pKₐ of phenol, there will be smaller fractions of phenol in the ionized form (Irene et al., 1998). This same result was identified in another research that used organophilic clay with chloride-hexadecyl-trimethyl-ammonium. This work used three pH values in the system clay-phenol, and they were 7.0, 8.3 (representing the natural state) and 9.0. The results indicated that at pH 7.0, there was better adsorption efficiency. The pKₐ of phenol is 9.95 (Teng & To, 2000), so when the pH of the system is below this value, the phenol is not completely disassociated with negative charges. However, the zeta potential of the organoclay was increasingly negative as the pH increases, so it is expected that there is at alkaline pH favoring the desorption process at equilibrium, due to electrostatic repulsion on the surface of the adsorbent (Cavalcanti et al., 2009).

3.3.2 Influence of temperature

It was found that the increased of temperature in the system clay-phenol, using 30°C and 40°C discourages the adsorptive process. At high temperatures there is a greater solubility of phenol in water, shifting the equilibrium towards of desorption (Cavalcanti et al., 2009). Using organoclay as adsorbent effluent derived from the stillage, such as phenol, dextran, glucose, fructose, glycerin and glycine, it was observed that the phenol appeared as the more adsorbed substance, in more low temperature, comparing 33°C and 43°C (Vianna et al., 2001).

4. Conclusion

According to several studies cited, it is possible to use effective organophilic clays as adsorbents for the removal of organic substances with high toxicity, such as phenols and BTEX compounds.
The smectite clays are formed by a region called interlayer region, endowed with various inorganic cations, giving it a hydrophilic nature. The replacement of inorganic cations by organic cations, through ion exchange, creates the organoclays, which are effective adsorbents of organic compounds, having many environmental and technological applications.

In addition to the structure and size of the quaternary ammonium ion, density and orientation of alkyl groups on the surface of the clays are determining factors in the interactions between modified clays and organic compounds. Consequently, the mechanisms that control these interactions depend on the type of cation that forms. The observations suggest the use of organoclays as adsorbents of organic compounds in contaminated water.

To obtain organophilic clays, the natural clays can be initially treated by replacement of your different cations, by sodium cation. And after, the organoclays can be treated by organic cations, such as quaternary ammonium.

Alterations in physicochemical adsorptive system, such as temperature and pH can to influence the efficiency of the process. It was seen that in some citations the decreased of pH favored the adsorptive process of phenol but did not changed significantly the adsorption of BTEX. In addition to pH, the increased of temperature also seemed to be relevant, shifting the equilibrium towards desorption, decreasing the adsorptive efficiency.

Among the isotherms that portray the adsorptive equilibrium, the Langmuir isotherm, Freundlich and Dubinin-Raduskevich were cited. For the adsorptive kinetic models, stand out the Lagergren, in models of pseudo-first order and pseudo-second order.

Alternative methods for removing harmful substances to the environment should be diffused and increasingly applied, decreasing the concentration of industrial effluents and decreasing costs.

5. References


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The petrochemical industry is an important constituent in our pursuit of economic growth, employment generation and basic needs. It is a huge field that encompasses many commercial chemicals and polymers. This book is designed to help the reader, particularly students and researchers of petroleum science and engineering, understand the mechanics and techniques. The selection of topics addressed and the examples, tables and graphs used to illustrate them are governed, to a large extent, by the fact that this book is aimed primarily at the petroleum science and engineering technologist. This book is must-read material for students, engineers, and researchers working in the petrochemical and petroleum area. It gives a valuable and cost-effective insight into the relevant mechanisms and chemical reactions. The book aims to be concise, self-explanatory and informative.

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