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Adsorption of Phenol and Dichlorophenols from Aqueous Solutions by Porous Clay Heterostructure (PCH)

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Abstract. Experiments have been conducted to examine the adsorption of phenol and dichlorophenols (2,5 DCP and 3,4 DCP) from water by a Porous Clay Heterostructure (PCH). Experiments were carried out for the analysis of adsorption equilibrium capacities using a batch equilibrium technique. The Freundlich adsorption model was best to describe adsorption equilibrium data for dichorophenols (r^2 = 0.994 for 3,4 DCP and r^2 = 0.993 for 2,5 DCP). In the case of the adsorption of phenol, the isotherm model of Langmuir was best to describe the experimental data (r^2 = 0.9839) at high equilibrium concentrations (0-500 ppm), while at low equilibrium concentrations (0-20 ppm) the Freundlich model was best to describe the data (r^2 = 0.9831). This deviation implies that the adsorption sites are heterogeneous. The adsorption capacity showed by the PCH for both phenol and DCPs from water (48.7 mg/g for 3,4-DCP, 45.5 mg/g for 2,5-DCP and 14.5 mg/g for phenol), suggests that the PCH have both, hydrophobic and hydrophilic characteristics, due to the presence of silanol and siloxane groups formed during the pillaring and preparation of the PCH.

Key words: clay, PCH, phenol adsorption, dichlorophenols adsorption.

Resumen. Se llevaron a cabo experimentos para estudiar la capacidad de adsorción de una Arcilla Porosa de Estructura Heterogénea para fenol y diclorofenoles (2,5 DCF y 3,4 DCF) en medio acuoso. Los experimentos de adsorción se realizaron por medio de una técnica por lotes para la determinación de las concentraciones en el equilibrio del adsorbato en solución. Las isotermas de adsorción para los diclorofenoles se ajustaron al modelo de la isoterma de Freundlich, obteniéndose un coeficiente de determinación de r^2 = 0.994 para el 3,4 DCF y r^2 = 0.993 para el 2,5 DCF. Para el caso de la isoterma de adsorción de fenol, el modelo de adsorción de Langmuir fue el que mejor se ajustó (r^2 = 0.9839) a concentraciones de equilibrio altas (0-500 ppm), sin embargo a concentraciones de equilibrio bajas (0-20 ppm), el modelo de Freundlich es el que mejor representa los datos (r^2 = 0.9831) implicando que los sitios de adsorción son heterogeneos. La presencia de capacidad de adsorción de la PCH tanto para fenol como para DCFs (48.7 mg/g para el 3,4-DCP, 45.5 mg/g para el 2,5-DCP y 14.5 mg/g para el phenol), sugiere la presencia de grupos siloxano y silanol en la PCH, los cuales fueron desarrollados durante la preparación y calcinación de ésta, confiriéndole así un carácter tanto hidrofílico como hidrofóbico a la superficie del adsorbente.

Palabras clave: arcilla, PCH, adsorción de fenol, adsorción de diclorofenoles.

Introduction

Many wastewaters contain significant levels of organic contaminants, which are toxic or otherwise undesirable because they create odor, unsightly color, foaming, etc. [1].

Among the different organic pollutants of aquatic ecosystems, phenols, especially the chlorinated ones, are considered as priority pollutants since they are harmful to plants, animals and human, even at low concentrations [2]. Owing to their extensive use, these compounds readily enter ecosystems, for example, by industrial and municipal waste water, by leachates emerging from waste deposits, by agricultural runoff of pesticides, by effluents from oil refineries, etc. [3,4]. Residues of chlorophenols have been found worldwide in soil, water and air samples, in food products, in human and animal tissues and body fluids. [5,6] Also, due to their slow degradation, chlorophenols, represent a major threat to ecosystems [7].

Since chlorinated phenols are not amenable to 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 [8,9]. Although activated carbons are among the most effective adsorbents and can be regenerated by thermal desorption or combustion of the pollutant in air, a substantial fraction of the carbon is lost with each regeneration cycle [10].

Due to the abovementioned, in the past years, there has been increasing interest in developing recyclable inorganic adsorbents, particularly of clay nature for efficient removal of organic pollutant from aqueous solutions [4,11].

Since the discovery of the Mobil Catalytic Material (MCMs) in 1992 [12], a lot of research has been conducted in mesoporous materials synthesized by a template mechanism involving the polymerization of a silica source around surfactant molecules [13]. In 1998, Pinnavaia [14] applied the MCM and Pillared Clay (PILC) preparation technologies on natural clays, obtaining a new interesting large-pore derivative, designated Porous Clays Heterostructure or briefly PCH. For this new solid, the silica source has been polymerized *in situ* between the aluminosilicate sheets and around micellar rods of surfactant and co-surfactant previously ion-exchanged on the interlayer space of the natural clay. After calcination for the removal of the organics, the mesopores are formed and the PCH obtained.

Characteristics common to the PCH materials are their high surface area (250-1000 m^2/g) and a combination of micro and mesoporosity. Also, in comparison to MCMs have important advantages such as their good thermal stability and mechanical strength [15].

Since the first preparation of the PCH material in 1998, research has been conducted mainly on studying its potentially function as heterogeneous acid catalyst (15-17). Also, derivatives of PCH have been reported such as a new class organic-inorganic hybrid PCH, prepared through the surfactant-directed assembly of organosilica in the galleries of montmorillonite [18].

Adsorption and pH dependent ion exchange capacities of PILCs and MCM materials (precursors of PCH materials) have been extensively studied [19-26], however, the adsorption properties of PCH materials have not yet been established. With this work the authors intend to contribute to the evaluation of PCH adsorption capacity of chlorophenols from aqueous solutions.

Experimental

PCH material. A PCH prepared and characterized as previously reported [27], was used in this work in order to study its adsorption capacity of phenol and dichlorophenols (DCPs) from aqueous solutions.

Adsorption isotherms. Phenol and dichlorophenols (2,5-DCP and 3,4-DCP) adsorption isotherms were obtained using the batch equilibrium technique reported by Tahani *et al.* [28]. The batch adsorption experiments were carried out in 40 mL glass bottles where 0.2 g of PCH and 25 mL of phenol or dichlorophenol aqueous solutions were added. Initial phenol or dichlorophenol concentration solutions ranged from 10-1000 ppm (pH was in the range of 5-6). The bottles were subsequently capped and shaken in an orbital-action shaker for 48 h at 25°C. Preliminary kinetic experiments demonstrated that adsorption equilibrium was reached within 48 h. At the end of the equilibrium period the bottles were taken off the shaker and the samples were left standing for a while to allow the adsorbent particles to settle. 10 mL of the supernatant was removed from the bottles with syringe and filtered through glass-fiber filter paper to remove any remaining adsorbent particles. Phenol or dichlorophenol equilibrium concentration was measured using a UV-VIS Perkin Elemer Lambda 3 spectrophotometer at an appropriate wavelength (Table 1). Linear calibration curves were used in the determination of equilibrium phenol and DCP concentrations. The curves were based on standards in the concentration range from 10-1000 ppm. Triplicate samples were run and the results averaged.

Table 1. Physicochemical properties of phenol and dicholrophenols [31].

Adsorbate	Wavelength of absorption, λ max (nm)	pKa	Solubility in water (ppm)
Phenol	269	9.89	66000
3,4 Dichlorophenol (3,4-DCP)	200	8.63	9256
2,5 Dichlorophenol (2,5-DCP)	230	7.51	2000

Results and Discussion

PCH. The preparation and characterization of the PCH were reported in a previous paper [27]. Table 2 shows a summary of the principal physicochemical characteristics of the PCH used. Specific surface area, average pore diameter and interlayer distance obtained for the PCH, are in good agreement to similar PCH products reported by other researchers as Pinnavaia [14] and Galarneau [15]. The characterization of the PCH by FTIR, TG and DSC analyses suggested [27] that the surface of the PCH shows a dual nature, hydrophobic due to the presence of siloxane groups (Si-O-Si) and hydrophilic due to the presence of silanol groups (Si-OH).

Adsorption of phenol and chlorophenols by PCH. Figure 1 displays the adsorption isotherms at 25°C, of phenol, 3,4-DCP and 2,5-DCP from aqueous solutions onto PCH. As can be seen, there is a marked higher adsorption for chlorophenols than that for phenol, reaching a maximum value of 48.7 mg/g for 3,4-DCP, 45.5 mg/g for 2,5-DCP and only 14.5 mg/g for phenol. The maximum adsorptions capacities obtained in this work were higher than those reported by Tahani *et al.* [28] for the adsorption of 2,6 DCP from water onto an Al-PILC (13 mg/g) and onto an Inorganic-Organic clay (IOC; quaternary amine-Al PILC) (29.2 mg/g); however, Srinivasan and Fogler [3] obtained an adsorption capacity of 97.2 mg/g for 3,5 DCP

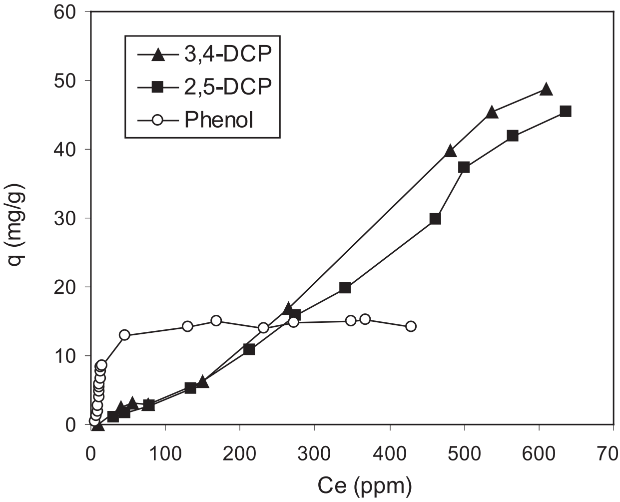

Fig. 1. Adsorption isotherms of phenol; 3,4-DCP and 2,5-DCP on PCH. **q**: adsorption capacity of the adsorbate per gram of adsorbent (mg/g); **Ce**: equilibrium concentration of the adsorbate (ppm).

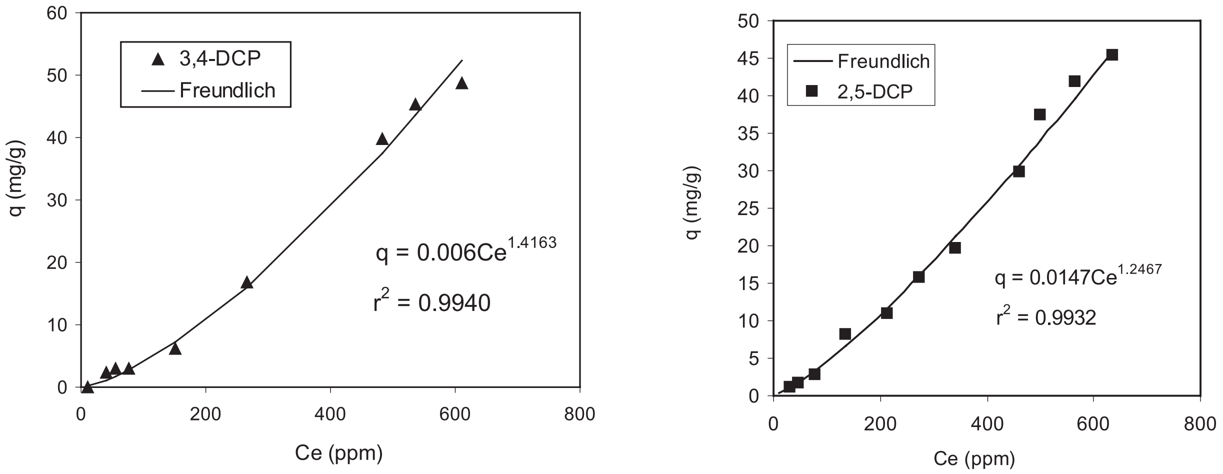

Fig. 2. Experimental adsorption isotherm of (**A**) 3,4-DCP and (**B**) 2,5-DCP onto PCH. Also shown is the Freundlich model. q: adsorption capacity of the adsorbate per gram of adsorbent (mg/g); **Ce**: equilibrium concentration of the adsorbate (ppm).

from water onto an IOC (cetyl-pyridinium-Al PILC), which is higher than the values obtained in this work, due to the highly hydrophobic nature of the intercalated cetylpiridinium and the retention of the chlorophenols *via* a partition mechanism rather than adsorption. The maximum adsorption capacity of 3,4-DCP obtained in the present work is similar to that reported by Yang [35] (52 mg/g) who used an exchange resin (amberlite XAD –2).

It has been reported that natural montmorillonite clays do not show adsorption capacity for chorophenols, being the contribution of physical adsorption by surface and edge groups of the silicate layers negligible [3]. Hence, the adsorption increment of DCP showed by the prepared PCH, can be attributed to the presence of the hydrophobic sites on the surface developed by siloxane groups of the intercalated SiO_2 pillars. In this way, the DCPs are mainly adsorbed by the benzene ring and chlorines groups onto the siloxane groups through Van der Waals forces and hydrophobic interaction. The shape of the DCPs isotherms shown in Figure 1 do not show the characteristic plateau of a monolayer in the range of concentration used, and were represented by the Freundlich isotherm model as shown in Figures 2A and 2B, with a determination coefficient r^2 of 0.994 for 3,4 DCP and $r^2 = 0.993$ for 2,5 DCP. The good correlation with the Freundlich isotherm model, suggests an exponential adsorption of these onto the PCH used.

The isotherm for phenol presented in Figure 1, although shows a maximum equilibrium adsorption concentration considerably lower than those obtained for DCPs, it was markedly higher than DCP in the range of 0-233 ppm Ce (equilibrium concentration of the adsorbate), suggesting the presence of hydrophilic sites on the PCH surface, of high affinity for the phenol molecules which are quickly saturated. This hydrophilic sites are very probable silanol groups from the intercalated SiO_2 pillars. This behavior contrasts with that reported for montmorillonite clays [30], silica [31], Al-PILCs and IOCs [28], where phenol from aqueous solutions is not adsorbed.

Figure 3 shows an expanded view of the adsorption isotherm of phenol in the range of 0-100 ppm, to show in detail the initial section of the isotherm. This figure shows a sigmoidal (S-shape) that reached a long plateau as the concentration increased. This isotherm can be classified as an S2 isotherm under the Giles *et al.* classification system [32] (cooperative adsorption) based on the initial shape of the isotherm. According to this classification, in S2 isotherms the more molecules of adsorbate are already adsorbed, the easier it is for additional amounts of adsorbate to become fixed to the surface of the adsorbent. This implies a side-by-side asso-

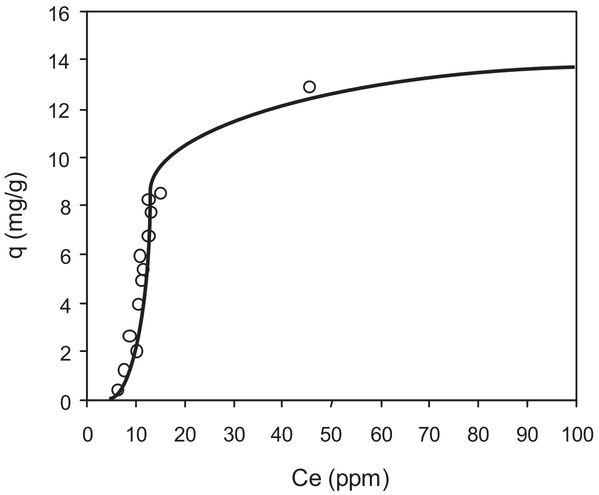

Fig. 3. Expanded view of the isotherm for phenol at low equilibrium concentrations (0-100 ppm **Ce**) onto PCH. **q**: solute adsorbed per gram of adsorbent (mg/g); **Ce**: equilibrium concentration of the adsorbate (ppm).

Tabla 2. Properties of the PCH used [27].

Property	PCH used
Unit cell formula	$Ca_{0.12}Na_{0.04}K_{0.04}{}^{*}Si_{0.48}(Si_8)(Al_{2.9}Fe_{0.20}Mg_{0.44})O_{20}(OH)_4$
Interlayer distance *d(001)* (Å)	23.2
BET Surface Area (m^2/g)	305.5
BJH, average pore diameter, (Å)	37.2

* Si as pillar.

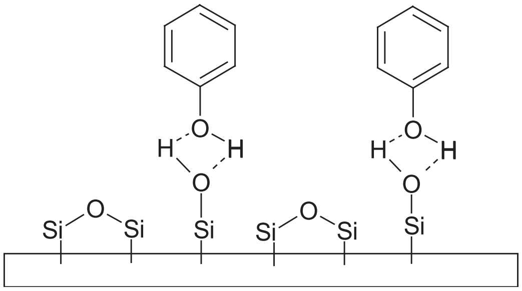

Fig. 4. Proposed adsorption mechanism of phenol molecules onto the surface of PCH, through hydrogen bonds between OH group of the phenol and the silanol groups of the PCH surface.

ciation between adsorbed molecules, helping to hold them to the surface and consequently making more stable the adsorbed layer. Molecules of adsorbate that show an S-shape isotherm (as in the case of phenol), are considered monofunctional, where the attraction towards the surface of the adsorbent arises from its OH group, giving an arrangement of adsorbed molecules oriented perpendicularly to the surface. Under the experimental adsorption conditions, the pH was in the range of 5 to 6, below the pKa of phenol (pKa = 9.89) (Table 1) and below the pKa for silica (pKa = 9.42) [33], therefore the phenol and the silanol groups of the surface of the adsorbent, were in a protonated form, making possible that the molecules of phenol were adsorbed onto the surface silanol groups through hydrogen bonds as illustrated in the Figure 4. This mechanism is similar to that reported for the adsorption of nitrophenol onto the surface of silica [33].

Figures 5A and 5B show the experimental adsorption isotherm of phenol from water onto PCH, the points represent experimental data, and lines represent the different isotherm models used. Langmuir and Freundlich models were used to represent the experimental data obtaining the following equations [1]:

Langmuir:

$$q = \frac{3.48\,Ce}{1 + 0.24\,Ce} \tag{1}$$

where:

q: adsorption capacity of the adsorbate per gram of adsorbent (mg/g).
Ce: equilibrium concentration of the adsorbate (ppm).

Freundlich:

$$q = 4.37 \times 10^{-3}\,Ce^{3.85} \tag{2}$$

where:

q: adsorption capacity of the adsorbate per gram of adsorbent (mg/g).
Ce: equilibrium concentration of the adsorbate (ppm).

The Freundlich model was the best to describe the adsorption equilibrium data at low concentrations (Figure 5B)

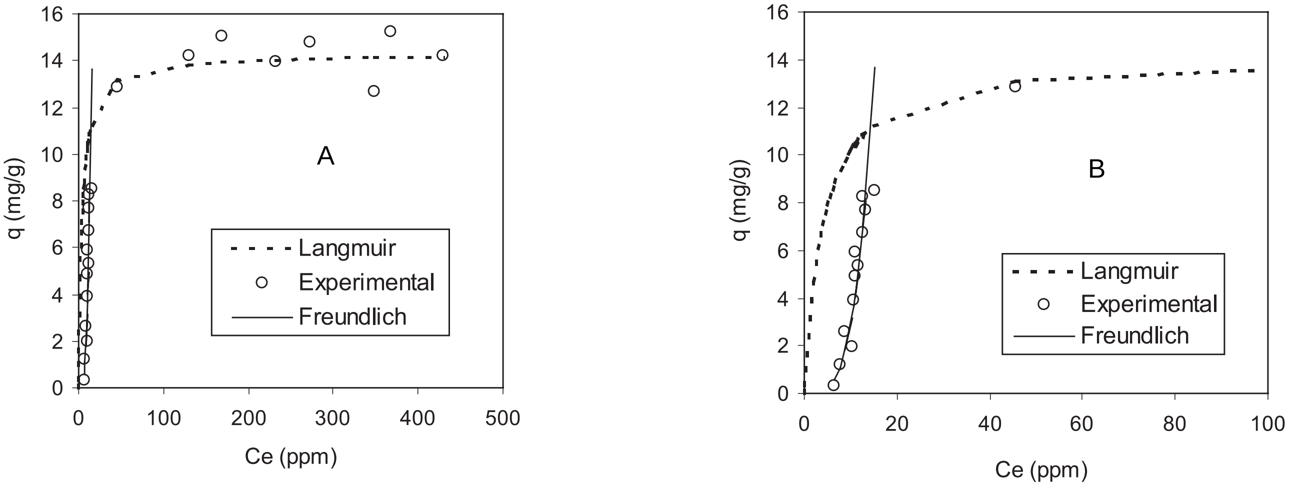

Fig. 5. Experimental adsorption isotherm for phenol onto PCH. Also shown are the isotherms models of Freundlich and Langmuir at (**A**) high equilibrium concentrations(0-500 ppm Ce) and (**B**) low equilibrium concentrations (0-100 ppm **Ce**). **q**: adsorption capacity of the adsorbate per gram of adsorbent (mg/g); **Ce**: equilibrium concentration of the adsorbate (ppm).

with $r^2 = 0.9831$ (equation 2), implying the presence of highly energetic sites were the molecules of phenol were adsorbed [34]. After the point of inflection of the experimental data, the Freundlich isotherm predicted that the equilibrium adsorption capacity should keep increasing exponentially with increasing equilibrium concentration in the liquid phase. However, the experimental adsorption isotherm for phenol presented a long plateau at higher equilibrium concentrations, implying the presence of a monolayer. Thus, Freundlich model should not be used for extrapolation of this data to higher concentrations.

Langmuir model (equation 1) gave a better fit at higher concentrations (Figure 5A) with a determination coefficient of $r^2= 0.9839$, implying the formation of a monolayer at higher concentrations, however, the deviation of this model at low equilibrium concentrations implies that the sites of adsorption on the surface of the adsorbent are heterogeneous.

Conclusion

The results of this study showed that the prepared PCH have adsorption capacity for the removal of phenol and dichlorophenols from aqueous solutions. The adsorption capacities showed by the PCH, suggests that it has both, hydrophobic and hydrophilic characteristics, due to the presence of silanol and siloxane groups formed during the pillaring and preparation of the PCH. These results are encouraging because they provide an indication that PCHs are capable of binding organic toxicant molecules which is otherwise extremely difficult to remove from aqueous waste streams.

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