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Hydrotalcite as a Potential Sorbent for the Removal of 2,4-Dichlorophenol

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Abstract

The removal of 2,4-dichlorophenol (DCP) using calcined and modified forms of hydrotalcite (HT) was studied. HT was calcined at 550 °C for 3 h. The calcined form (HTC) was modified under argon atmosphere using sodium stearate in an amount equivalent to 100% of the theoretical anion exchange capacity of HT. The 3 forms of HT were subjected to X-ray diffraction analysis. It was determined that the peak with characteristic basal spacing d = 7.62 Å corresponding to interlayer carbonate anion disappeared in HTC and a peak with d = 32 Å confirming the adsorption of stearate anion appeared in organo-HT. Adsorption equilibria of DCP on HT and organo-HT were measured using batch equilibration. Adsorption behavior was modeled by the modified Freundlich equation. It was determined that HTC and organo-HT have maximum efficiencies corresponding to certain initial concentrations, i.e. 2.76 mmol/l for HTC and 3.68 mmol/l for organo-HT. At these concentrations, HTC and organo-HT can adsorb 61% and 17% of DCP, respectively.

Key words: Hydrotalcite, Organo-hydrotalcite, 2,4-Dichlorophenol, Adsorption isotherm, Sodium stearate-hydrotalcite complex.

Introduction

Phenolic compounds exist as harmful and toxic chemicals in wastes containing plastics, leather and paint and in many industrial effluents such as those from oil refineries. Since they are not amenable to biodegradation except at very low concentrations, other methods such as chemical oxidation, coagulation, chlorination, solvent extraction, liquid membrane permeation and adsorption are commonly used for their removal (Juang *et al.*, 1996; Özbelge *et al.*, 2002). Adsorption, a relatively simple and inexpensive method, appears to offer the best prospects.

Although the use of naturally occurring adsorbents is the general trend of research (Viraraghavan and de Mario Alfaro, 1998; Banat *et al.*, 2000; Şişmanoğlu and Pura, 2001), properties such as small and non-homogeneous pore size distribution, and weak hydraulic characteristics restrict their versatility. Hydrotalcite (HT) having a positively charged layered brucite related structure is rare in nature but easy to prepare (Reichle, 1986). In HTs, positive charges, through the replacement of Mg by Al, are neutralized by interlayer anions such as carbonate, nitrate, hydroxide and chloride. Although CO_3^{2-} is the anion that nature prefers, other anions can also be introduced if air is excluded from the synthesis. The interlayer anions can also be replaced by other organic and inorganic anions (Villa *et al.*, 1999). HT is calcined at 500-800 °C to form magnesium and

aluminum oxide solid solutions. The solution has a memory effect and therefore it is possible to reconstruct the original HT from aqueous solutions containing anions (Vaccari, 1998).

In general, the properties of clay minerals used as adsorbents can be improved through modification. Modified clay can have hydrophobic surfaces, extended interlayer distance, and optimized rheological behavior, and for these purposes, the use of clay mineral/surfactant complexes is very common (Dekany *et al.*, 1996; Li and Bowman, 1998; Li and Rosen, 2000; Koh and Dixon, 2001; Shen, 2002). There are few reports on the adsorption of surfactants on HT to form a surfactant HT complex and the application of this complex as an adsorbent (Dekany *et al.*, 1997; Villa *et al.*, 1999; Klumpp *et al.*, 2004). Sodium dodecyl sulfate (SDS) is generally used in the modification but Klumpp *et al.* (2004) modified HT with sodium bis (2-ethylhexil) sulfosuccinate, AOT, and they found this complex to be an effective adsorbent in the removal of 2,4-dichlorophenol.

In this work, the adsorption equilibria of DCP were measured over a wide concentration range (1.8×10^{-5}-3.7×10^{-3} mol/l) on both the calcined HT (HTC) and sodium stearate-HT complex and the adsorption behavior was modeled using the modified Freundlich equation (Urano *et al.*, 1981). To our knowledge, the use of sodium stearate-HT complex in the removal of DCP or any other nonionic organic compound has not been reported before.

Experimental

Preparation of calcined HT

The Al/Mg weight ratio of HT purchased from Sud-Chemie, Germany, was equal to 0.53 and the physical properties are given in Table 1. To prepare the calcined form, HT was heated from room temperature to 550 °C over 2 h and then maintained at this temperature for 3 h. The HTC was cooled to 200 °C and placed in a desiccator under argon atmosphere.

Modification

A suspension was prepared by adding 140 g of HTC to 5 l of water at 80 °C. The solution containing sodium stearate in an amount equivalent to 100% of the theoretical anion exchange capacity, which is about 4 mmol/g, was added to the suspension. Since a positive charge occurs as a result of the replacement of Mg^{2+} by Al^{3+}, the theoretical anion exchange capacity is actually equal to the number of moles of Al^{3+} and it was calculated from the chemical composition of the HT used. The reaction was completed followed by mixing at 80 °C for 24 h. The reaction mixture was cooled to room temperature; the solid and liquid phases were then separated. The organo-HT was washed repeatedly to remove residual sodium stearate and then subjected to freeze drying.

Table 1. Typical analysis of hydrotalcite used.

Constituent	Value
Al_2O_3, weight %	20.5
MgO, weight %	34
CO_2, weight %	9.5
pH (5% suspension in water)	10
Moisture Content (120 °C)	Max 3%
Density	2100 kg/m^3
BET Surface Area	$\leq$ 17 m^2/g
Particle Size Distribution	
50%	<0.4 μm
90%	<1.0 μm
10%	<0.2 μm

Adsorption measurements

Adsorption measurements were conducted using batch equilibration as follows. HT was weighed and transferred into polypropylene tubes. A known concentration of 2,4- dichlorophenol solution was then added to the tubes and they were closed tightly. The tubes were shaken for 24 h at 20 °C. Supernatants separated by centrifuging at 20,000 rpm were analyzed in a UV spectrophotometer. Linear calibration curves were used in the determination of equilibrium DCP concentrations. The curves were based on standards in the concentration range from 1.8×10^{-5} to 3.7×10^{-3} mol/l. In all cases, the coefficient of determination exceeded 0.99.

X-Ray diffraction

The X-Ray diffraction patterns of HT, HTC and organo-HT were recorded on a Seiffert 3000 θ/θ diffractometer using CuK_α radiation. During measurements, samples smoothed on glass slides were covered with Mylar film to avoid moisture and CO_2 uptake.

Results and Discussion

Characterization of adsorbents

HT, HTC and organo-HT were subjected to physical and chemical analyses to see the changes in their chemical composition and crystal structure. The carbon content of HT, HTC and organo-HT were 9.5, 1.28 and 28.5%, respectively. A comparison of these values reveals that CO_3^{2-} was almost removed at the end of calcination and the stearate anion was exchanged in the structure.

Although HT crystallinity can be maintained up to 600 °C depending on the Al/Mg ratio (Lopez *et al.*, 1997), XRD analyses were conducted to determine whether the heat treatment caused any collapse in the structure except for the removal of CO_3^{2-}. The results are given in Figures 1 and 2 for HT and HTC, respectively. A comparison of the figures reveals that HT and HTC have the same pattern except for the diffraction peak, with the characteristic basal spacing d = 7.62 Å corresponding to interlayer CO_3^{2-} (Reichle, 1986). The similarity of the patterns and the disappearance of the peak confirm that CO_3^{2-} is removed from the interlayer without causing any collapse in the crystal structure.

In order to confirm the adsorption of stearate in the interlayer, X-ray diffraction was also applied to organo-HT. Figure 3 shows the X-ray diffraction pattern of the HT-surfactant complex with a diffraction peak of 32 Å verifying the presence of the stearate anion in the HT interlayer.

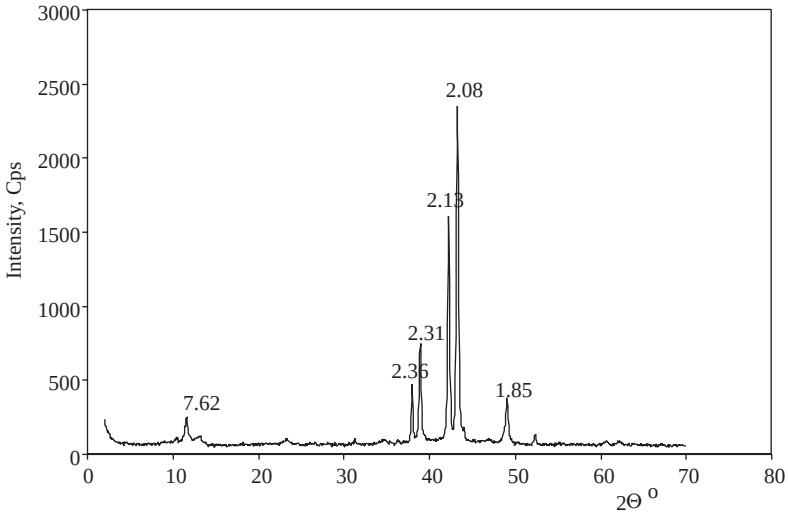

Figure 1. XRD pattern of original HT.

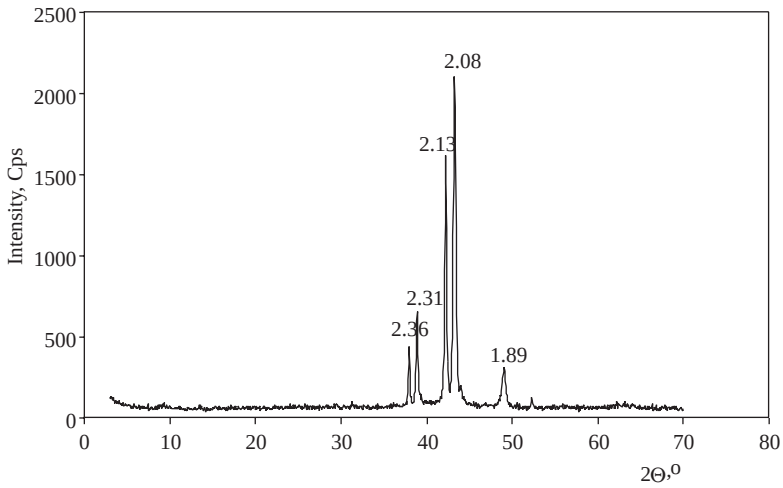

Figure 2. XRD pattern of HTC.

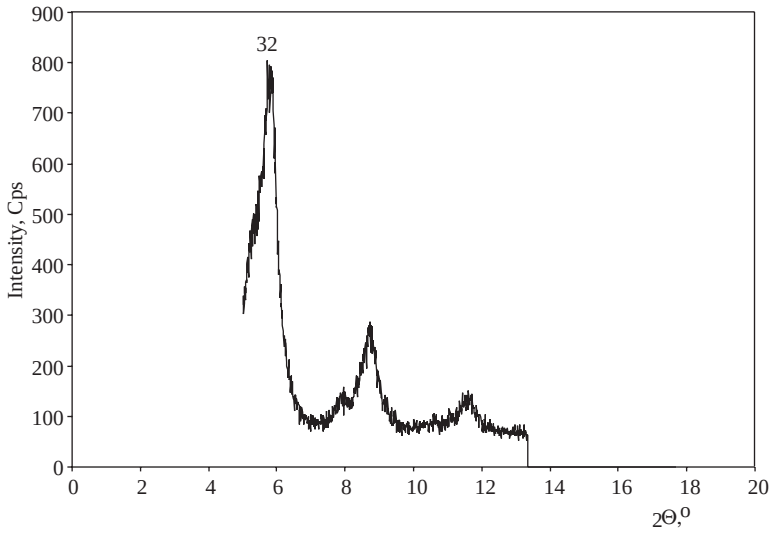

Figure 3. XRD pattern of organo-HT.

Adsorption behavior

Adsorption isotherms of DCP on HTC and organo-HT are given in Figures 4 and 5, respectively. The shapes of the isotherms are rather different: 2 inflection points are observed in the adsorption isotherm of DCP on HTC. In the case of organo-HT, the convex isotherm exhibits a smooth increase in comparison with the adsorption isotherm of DCP on HTC. The difference observed in the adsorption isotherms is attributed to different adsorption mechanisms appearing as a result of the different surface structures and ionization behavior of DCP. Phenol and its derivatives are actually ionizable organic compounds. They dissociate into phenolate and a proton depending on the pH. During the experiments, the pH of the adsorption medium was 9, and a significant part of the DCP molecules is present as phenolate (pKa = 7.8) at this pH. Since carbonate anions were removed by calcination, phenolate can easily intercalate into the positively charged HT surface. As mentioned before, calcined HT is actually magnesium and aluminum oxide solid solution with a memory effect. This effect induces the reconstruction of the original HT structure from aqueous solutions by taking anions. Therefore, phenolate will participate in the reconstruction of HT and adsorption takes place during the reconstruction. Hermosin *et al.* (1996) also reported the same behavior. They proposed that phenolate participates in the reconstruction of HT according to the following reaction:

$$Mg_3AlO_4(OH) + 4H_2O + PhO^- \rightarrow$$
$$[Mg_3Al(OH)_8]\ (PhO) + OH^-$$

In the case of adsorption on organo-HT, DCP is adsorbed only in molecular form. As confirmed by XRD analysis, stearate anions participate in the reconstruction of HT during the modification. The intercalation of stearate anions into the interlayer of HT causes the formation of a hydrophobic layer repelling water and therefore ions from the surface. Since the amount of stearate used is equivalent to 100% of theoretical anion exchange capacity, all positive charges are neutralized and thus the surface charge decreases to zero. Under these circumstances, the adsorption of phenolate on the organo-HT surface is not probable. Therefore, the hydrophobic sorption mechanism will be dominant and DCP will be adsorbed in molecular form. The adsorbed amounts seem to reach a plateau at approximately 0.2 mmol/g, as shown in Figure 5. This amount is close to the 0.3 mmol/g reported by Klumpp *et al.* (2004) for the adsorption of DCP on AOT-HT complex, although the surfactant load, 4 mmol/g, is 16 times greater in our work. By considering the increase in adsorbed amounts depending on the improvements in wetting behavior with decreasing surfactant loads (Klumpp *et al.*, 2004), it can be concluded that sodium stearate- HT complex can be as good as AOT-HT complex for the adsorption of DCP.

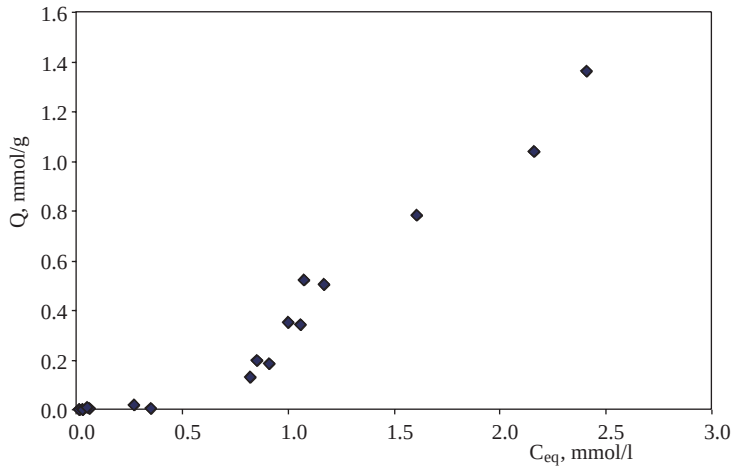

Figure 4. Adsorption isotherm of DCP on HTC.

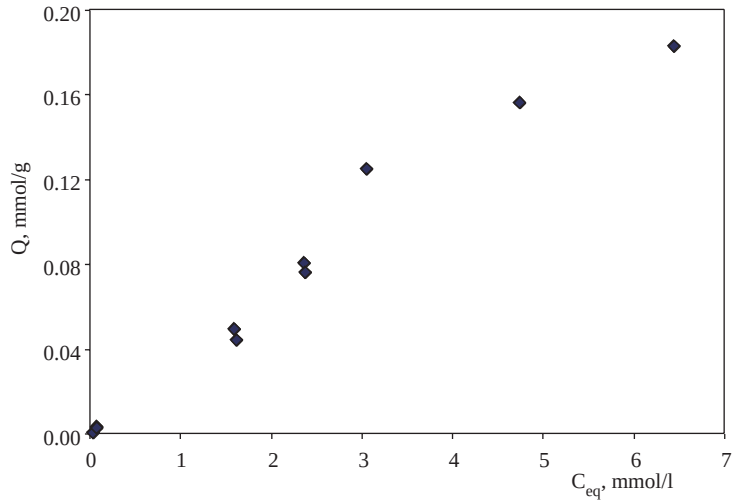

Figure 5. Adsorption isotherm of DCP on organo-HT.

The adsorption of many adsorbates can be defined by the Freundlich equation but the adsorbed amount seems to increase to infinity with the conventional form of the equation (Urano *et al.*, 1981). This issue can be handled through the modification of the Freundlich equation and the modified form is defined as the relationship between adsorbed amount and reduced concentration;

$$Q = k'(C/C_s)^{1/n} \tag{1}$$

where C is the molar concentration of adsorbate in solution at equilibrium and k′ is the limiting adsorbed amount at the saturation concentration of adsorbate.

The parameters of the modified Freundlich equation with correlation coefficients are tabulated in Table 2. A comparison of the k′ values reveals that HTC is more effective than organo-HT in the removal of 2,4-dichlorophenol.

Table 2. Parameters of modified Freundlich equation.

	k′	n	r
HTC	0.0604	0.61	0.959
Organo-HT	0.00094	0.98	0.995

The relation between the molar adsorbed amount and equilibrium adsorption potential is given as (Urano *et al.*, 1981)

$$Q = k' \exp(-E_{eq}/nRT) \tag{2}$$

The change in equilibrium adsorption potential with adsorbed amount is shown in Figure 6. Although the adsorption potentials of adsorbents seem nearly the same at low Q values, they differ with increasing adsorbed amounts. Since the liquid phase is the same in both cases, this difference in adsorption potentials also points to different adsorption mechanisms.

Adsorption efficiency

Adsorption efficiency is defined in this work as the ratio of the amount of DCP removed to the maximum amount that can be removed at the same initial concentration. The efficiencies of adsorbents are given in Figure 7 as a function of initial bulk concentration. HTC is more efficient and an increase in the adsorption efficiency is observed for both cases. If adsorption is considered to be a simple equilibrium reaction occurring as a result of the partition of adsorbate between liquid and solid phases and the effects of all other parameters except temperature are omitted, this behavior is expected. Since the coefficient of equilibrium remains constant at constant temperature, the adsorbed amount will increase in parallel with the increase in initial concentration. However, the observation of a slight decrease in efficiencies reveals that the surface saturation must also be taken into account.

The observation of a maximum in each case implies that the adsorbents should be used in the removal of DCP from aqueous solutions in which the initial DCP concentrations are in the vicinity of the maximum efficiencies. Therefore, the use of HTC in the concentration range from 1.47 mmol/l to 5.47 mmol/l will be appropriate. This range is from 9.2 $\times 10^{-2}$ mmol/l to 7.36 mmol/l for organo-HT.

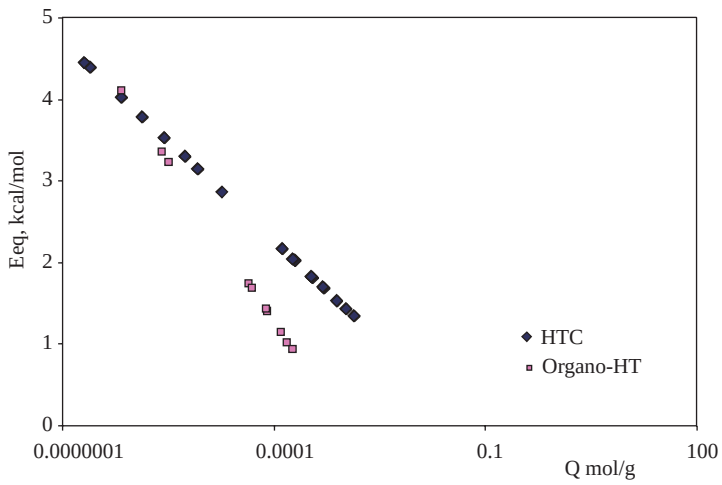

Figure 6. The change in equilibrium adsorption potentials (T = 293 K).

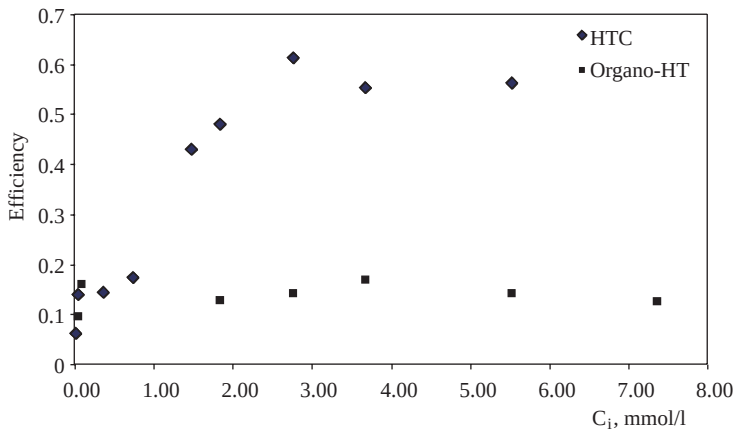

Figure 7. Efficiencies of adsorbents.

Conclusion

The results of the study showed that HTC is a good adsorbent for DCP. It can adsorb DCP to the extent of 61% and the adsorption takes place during the reconstruction of HT.

In the case of organo-HT, the hydrophobic sorption mechanism is dominant. This result implies that organo-HT will be an effective adsorbent in wastewaters with low pH values, such as olive mill effluents (Al-Malah *et al.*, 2000).

List of Symbols

C	concentration mol/l
C_s	solubility mol/l
k′	constant mol/g
n	constant
pK_a	logarithm of equilibrium constant
Q	adsorbed amount mol/g
r	correlation cofficient
R	gas constant cal/mol K
T	temperature K
2θ	angle of incidence of X-ray

Abbreviations

cps	count per second
DCP	2,4-dichlorophenol
HT	hydrotalcite
HTC	calcined hydrotalcite
AOT	sodium bis (2-ethylhexil) sulfosuccinate (aerosol T)
AOT-	HT aerosol T-hydrotalcite

Subscripts

eq	equilibrium
i	initial

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