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Removal of Phenol by Using Montmorillonite, Clinoptilolite and Hydrotalcite

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Abstract. This work is to study the removal of phenol from aqueous solutions by adsorption using three different adsorbents, clinoptilolite, montmorillonite, and hydrotalcite (HT). Except for montmorillonite, the other adsorbents were treated. Clinoptilolite was modified using cetyltrimethylammonium bromide (CTAB) and hydrotalcite was calcined by heating to 550°C. Adsorption isotherms of phenol on all of the mentioned adsorbents was determined by using the batch equilibration technique and indicated that, the adsorption behavior could be modelled by using the Modified Freundlich equation. The differences observed in the isotherms were explained by the variations in adsorbent-adsorbate interactions under the effects of the different surface structures of adsorbents and the pH dependent ionization behavior of phenol. Calcined hydrotalcite (HTC) was found to be the best among the studied adsorbents since it can adsorb 52% of phenol from a solution containing initially 1 g/L phenol for the 1/100 adsorbent solution ratio while the others can adsorb only 8% of phenol for the same concentration and adsorbent solution ratio.

Keywords: montmorillonite, clinoptilolite, hydrotalcite, organic pollutant, phenol, adsorption

Introduction

Deterioration in soil, surface and ground water qualities due to existence of organic pollutants promotes the research, targetting environmental protection in two ways: (1) to develop environmentally safe technologies and (2) to remove the pollutants by economical and efficient techniques. Adsorption, as a simple and relatively economical method, is a widely used technique in the removal of pollutants. Although the adsorbents used may vary due to the change in adsorption conditions depending on the type of pollutants, the properties affecting the efficiency of an adsorbent are; a large surface area, the homogeneous pore size, well defined structural properties, selective adsorption ability, easy regeneration, and multiple use. Since the synthetic adsorbents satisfying most of these conditions are relatively expensive, use of natural adsorbents is an active area of research (Banat et al., 2000; Brownawell et al., 1990; Shen, 2002; Sismanoğlu and Pura, 2001; Viraraghavan and de Mario Alfaro, 1998; Wu et al., 2001).

Clays and zeolites are aluminosilicate minerals with negatively charged surfaces. Although the same elements are included in their compositions, their crystal structures are quite different. Montmorillonite is a member of the smectic clays with layered structure and exhibits a swelling behavior resulting from the weak attraction between the oxygens on the bottom and top of the tetrahedral sheets (Grim, 1968). This property allows the exchange of neutralizing cations with cationic surfactants and the surface can be covered with a hydrophobic layer converting the competition in favor of nonpolar compounds. Clinoptilolite is the most abundant natural zeolite (Sismanoğlu and Pura, 2001). It has a cage-like structure with the largest aperture measuring 4.4 by 7.2 Å and is free

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of the shrink-swell behavior. Its surface chemistry can also be altered through treatment using cationic surfactants. In contrast to montmorillonite, however, the surface treatment is limited to the external surface of the zeolite particles if the surfactant is larger than the largest aperture of zeolite. Beside the conversion of the external surface from hydrophilic to hydrophobic, it is also possible to change the external surface charge from negative to positive by covering the surface with a surfactant bilayer (Li et al., 2000). For these reasons, the use of surfactant modified zeolites is very common in the removal of various pollutants including anions and ionizable organic compounds (Bowman et al., 1995; Haggerty and Bowman, 1994; Li and Bowman,1997; Li et al., 1998, 2000).

Hydrotalcite commonly used as catalyst and catalyst precursor, or in medical applications is rare in nature but simple and relatively inexpensive to prepare in the laboratory (Reichle, 1986). It is a member of Layered Double Hydroxides (LDHs) having a structure related to brucite $Mg(OH)_2$. The substitution of Al^{3+} for Mg^{2+} creates a net positive charge neutralized by mono- or divalent anions such as carbonate, nitrate, hydroxide and chloride. Although carbonate is the anion that nature prefers (Reichle, 1986), other anions can also be introduced only if air is excluded from the synthesis. LDHs have good anion exchange capacities, high surface area and a memory effect (Vaccari, 1998). This effect gives superiority to LDHs as potential sorbents for anions, since the calcined product can rehydrate and reconstruct the original layered structure from aqueous solutions containing anions (Klumpp et al., 2004; Yapar et al., 2004).

Phenol and its derivatives are the priority pollutants since they are toxic and harmful to organisms even at low concentrations. Beside their toxic effects, phenolic compounds create an oxygen demand in receiving waters, and impart taste and odour to water with minute concentrations of their chlorinated compounds. Surface and ground waters are contaminated by phenolics as a result of the continuous release of these compounds from petrochemical, coal conversion and phenol producing industries. In addition to these industries, olive oil production is another source for the release of phenol due to the high phenol content of olive mill effluents. Because of the above mentioned issues, the removal of phenol is an active area of research. Although the research on the removal of phenol and its derivatives by adsorption is abundant, only few of them is about the use of modified zeolite and HT as adsorbents (Hermosin et al., 1993, 1996; Klumpp et al., 2004; Li et al., 2000; Yapar et al., 2004). The goal of these studies is generally removal of phenol derivatives instead of phenol. The objective of the present research is to remove phenol from aqueous solutions using montmorillonite, organo-clinoptilolite, and calcined hydrotalcite.

Materials and Methods

Materials Used

A typical analysis of the montmorillonite obtained from the ReŞadiye mine of Turkey is given in Table 1. Ironoxide and silica were removed by differential sedimentation technique. The removal of these impurities was followed by drying the material at 60°C for 96 h. After being dried at 60°C, it was pulverized to pass through a 530 μm sieve.

Clinoptilolite was obtained from the Bigadiç mine of Turkey and its typical analysis is given in Table 2. Clinoptilolite was washed repeatedly with pure water at 60°C to remove the water soluble residues and dried at 160°C before use.

Hydrotalcite purchased from Sasol GmbH was calcined by heating the material to 550°C for three hours. Table 3 shows the typical analysis of hydrotalcite given by the manufacturer.

Cetyltrimethylammonium bromide was purchased from Aldrich Milwaukee and all the reagents used were of an analytical grade.

Table 1. Typical analysis of montmorillonite.

Constituent	Value
SiO_2	57.70
Al_2O_3	22.17
Fe_2O_3	3.80
Na_2O	2.71
K_2O	1.18
CaO	2.57
MgO	1.83
KK*	7.31
BET surface area, m^2/g	29.57
CEC,** meq/100 g	91
Average pore half width (Å)	20
Particle size (μ)	<530

*Weight loss between 700–1000°C.

**Cation exchange capacity determined through sodium acetate method.

Table 2. Typical analysis of clinoptilolite.

Constituent	Value
SiO_2	78.05
Al_2O_3	6.34
Fe_2O_3	0.45
Na_2O	2.57
K_2O	1.82
CaO	2.31
MgO	0.33
H_2O	8.14
BET surface area (m^2/g)	28.69
External surface area (m^2/g)	20.57
Average pore half width (Å)	19.3
Particle size (μ)	500–1000

Table 3. Typical analysis of HT.

Constituent	Value
Al_2O_3, wt%	39.5
MgO, wt%	60.5
Carbon content, wt%	2.5
BET surface area (m^2/g)	17.0
Particle size (μ)	13.80
Average pore half width (Å)	25.6

Properties given by manufacturer.

Characterization of Adsorbents

All the adsorbents were subjected to X-ray diffraction analyses using a Jeol 15 DX 100 S_4 X-Ray Diffraction Spectrometer with Cu K_α radiation.

The BET surface area and average pore half width of natural adsorbents were determined by nitrogen adsorption using an OMNISORP 100 CX.

Adsorption of CTAB on Clinoptilolite

The external cation exchange capacity, ECEC, of zeolite was determined to be 13.87 meq/100 g of zeolite by a procedure similar to Ming and Dixons' (1987).

The batch equilibrium isotherm was determined by adding 0.1 g of clinoptilolite to 100 ml of the solutions containing the surfactant in amounts equivalent to various percentages of the ECEC. The suspensions were shaken for 24 h at 20°C and then were centrifuged 5 min at 5000 rpm. Concentrations of supernatants were determined through the methyl orange method (Wang and Langley, 1975). This method involves complexation of cationic surfactant with methyl orange at acidic condition, chloroform extraction and water-chloroform phase separation is followed by spectrophotometric measurement. The measurements were carried out in a JASCO 7000 UV spectrophotometer at the absorption wave length of 401 nm.

Preparation of Organo-Clinoptilolite

Zeolite was added to the aqueous solution containing CTAB in an amount equivalent to 193% of ECEC. The mixture was stirred for one hour at 50°C and then was allowed to cool and settle. After the separation of solid and solution phases, modified zeolite was washed first with a 50% ethanol water solution then with distilled water several times to remove residual CTAB. Modified zeolite was made ready for the adsorption experiments by drying for 96 hours at 40°C.

Phenol Adsorption Isotherms

Phenol adsorption isotherms from aqueous solutions were obtained using the batch equilibration technique. 1 g of adsorbents were added to 100 ml of the unbuffered solutions in a concentration range from 0.5 to 6 g/L. The concentration range was chosen by considering the high phenol content of olive mill effluents. Suspensions shaken for 24 h, were placed in polypropylene tubes and then centrifuged. Supernatants collected in dark brown colored bottles were analyzed by gas chromotoghraphy using a HP 5980/series 2 gas chromatograph. Linear calibration curves were based on standarts in the concentration range of 0.5 to 6 g/L. In all cases, the coefficients of determination exceeded 0.99.

All experiments were carried out at least two times and an average was taken for each point on the isotherm.

Results and Discussions

Characterization of Adsorbents

The X-ray diffraction pattern of montmorillonite is given in Fig. 1. The basal spacing was measured as 11.95 Å. This value is close to the basal spacing of montmorillonite having Na^+ ions in the interlayer space with one molecular water layer (12.5 Å). Chemical analysis given in Table 1 coincides with this idea by proving that the exchangable cations between the silicate layers are composed primarily of Na^+ ions. Due to

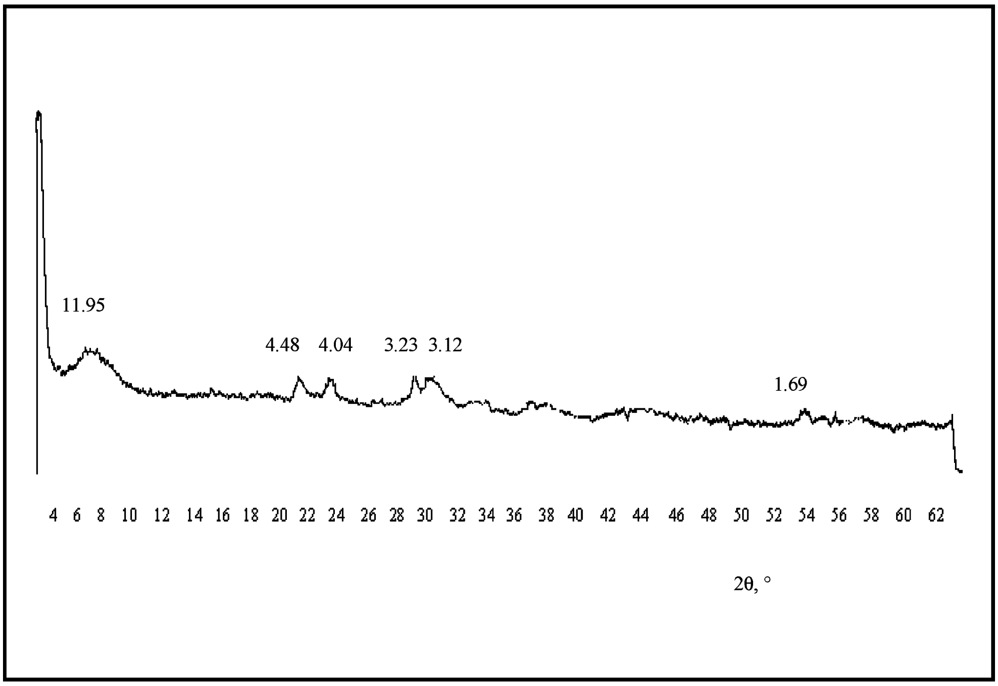


Figure 1. XRD pattern of montmorillonite.

its large surface area and swelling property, montmorillonite was used without applying any surface treatment.

By considering all the factors mentioned previously, clinoptilolite surface was modified using CTAB. X-ray diffraction patterns of crude and modified forms are given in Fig. 2. A comparison of the patterns reveals that modification causes no change in the crystal structure.

The average pore diameter of clinoptilolite was found to be 38.6 Å and according to Dubinin's classification, clinoptilolite has mainly mesopores (Oscik, 1982) and the ratio of external surface to total surface area is high. Since quaternary ammonium surfactants adsorp on the external surface, the high external surface area relative to total area forms an advantage in the modification.

The characteristic peaks of hydrotalcite, brucite, and aluminum are given in Table 4. These peaks are observed on the XRD pattern given in Fig. 3(a). In Fig. 3(b), the diffraction peaks characteristic of hydrotalcite and brucite disappear. This result points the destruction of the crystal structure, in addition to the removal of carbonate since the diffraction peak with basal spacing $d = 7.69$ Å corresponds to the interlayer CO_3^{2-} anion (Reichle, 1986). The remaining peaks are the characteristic of an Al and Mg mixed oxide (Hermosin et al., 1996).

Table 4. Characteristic peaks of hydrotalcite, brucite and aluminum appearing on their XRD patterns.

Mineral	X-ray diffraction by intensity (I/I_o)*		
Hydrotalcite	7.690 (1)	3.880 (0.7)	2.580 (0.2)
Brucite	2.365 (1)	4.770 (0.9)	1.794 (0.55)
Aluminum	2.360 (1)	1.224 (0.9)	2.040 (0.7)

*Taken from http//:webmineral.com.

Adsorption Behavior

The adsorption of phenol on montmorillonite at around a pH of 8 is given in Fig. 4. Two regions are observed in the figure. In the first region, the increase in the adsorbed amount continuing up to 1.765 g/L are followed by a plateau region. A smooth increase in the adsorbed amount with equilibrium bulk concentration is observed in the last part of the curve. A similar behavior was also observed in the adsorption of phenol on montmorillonite at a pH of 5.5 (Yılmaz and Yapar, 2004). In this work, the pH of suspensions were adjusted using an acetic acid/ sodium acetate buffer and no considerable difference were observed between the pH values measured before and after adsorption.

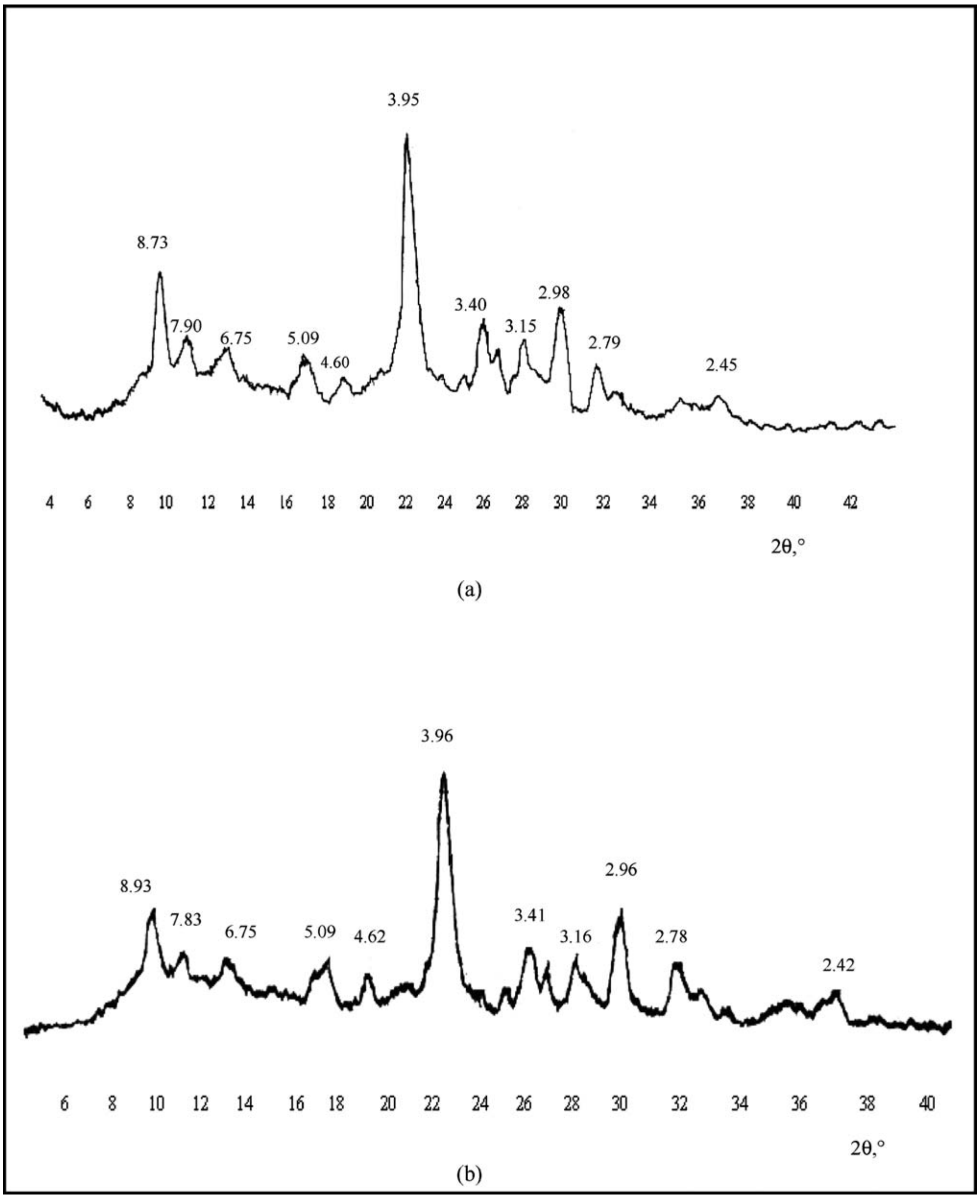
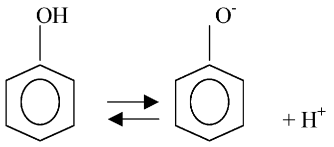


Figure 2. XRD patterns of clinoptilolite, (a) crude and (b) modified.

Adsorption isotherms of phenol on organo-clinoptilolite at around a pH of 7 and on calcined hydrotalcite at around a pH of 9 are given in Figs. 5 and 6, respectively. Although almost the same trend is observed in both curves, in the case of organo-clinoptilolite the adsorbed amount continues to increase slightly.

The differences observed in the adsorption behaviors of adsorbents are attributed to the effect of the ionization behavior of phenol in addition to the different surface structures. Phenol can dissociate to phenolate and a proton according to the following reaction.



The ratio of phenol to phenolate is the function of pH at a constant temperature. Therefore adsorption

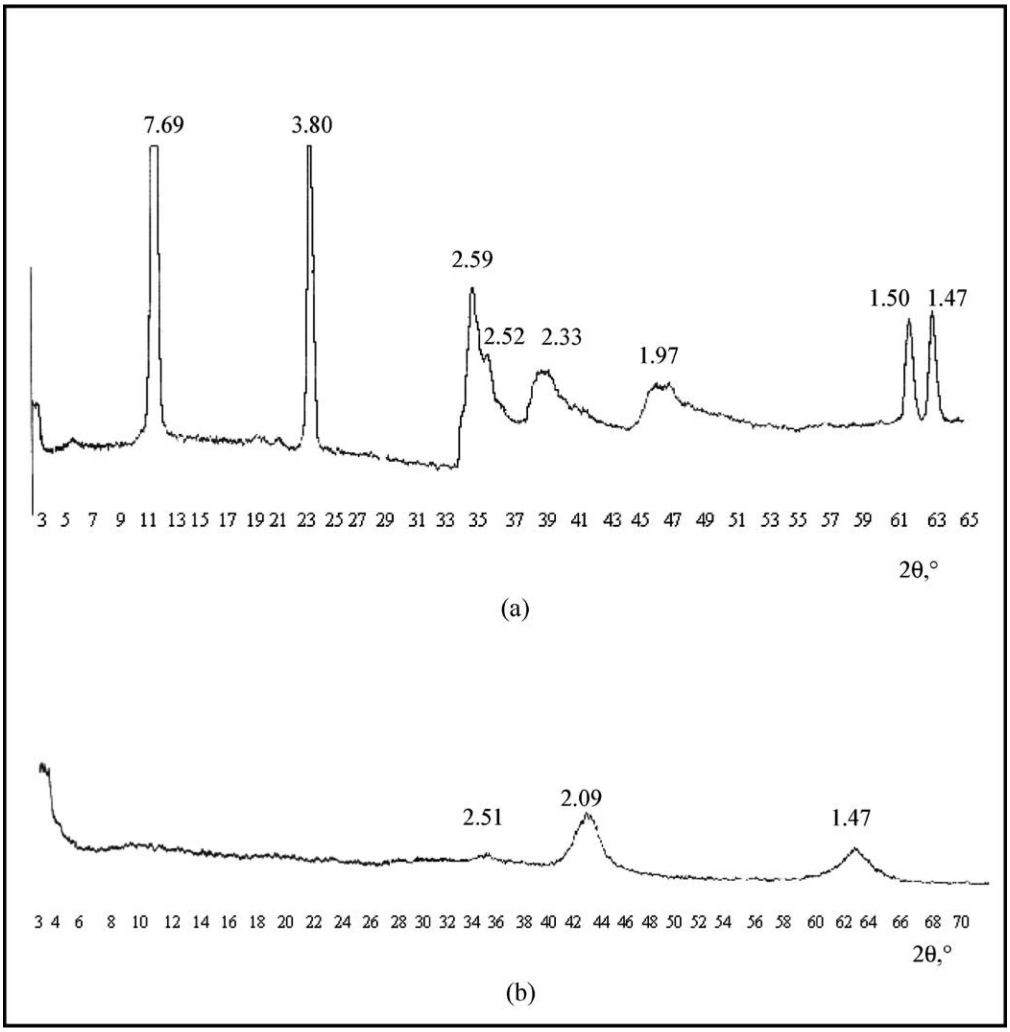


Figure 3. XRD patterns of hydrotalcite, (a) original and (b) calcined.

proceeds through the polarization of π-electrons and anion exchange. Phenol exists mainly in a neutral molecular form when the pH value equals 3-8 (Wu et al., 2001) and adsorption through polarization of π-electrons will be dominant in this range in contrast to adsorption by anion exchange at high pH values.

Adsorption of Phenol on Montmorillonite

The ionic fraction of phenolate at a pH of 8 and 9 is 0.016 and 0.13, respectively. Under these conditions, it is possible for the adsorption of phenol on a negatively charged surface through the polarization of π electrons and phenolate on the edges of montmorillonite through the ion exchange. In the case of phenolate, the adsorbed amount will not be comparable to the adsorption of the phenol molecule since the anion exchange sites of montmorillonite are very limited and the amount of phenolate is very low. Since phenol molecules interact strongly with water through the hydrogen bonding promoted by the dipol moments of the molecules, the water and phenol, adsorbed amounts depend on the relative magnitudes of water-phenol and phenol-surface interactions. The effect of water-phenol interaction will be dominant in low concentrations but it will diminish by increasing concentration due to the decrease in the number of water molecules which are available for hydrogen bonding. Thus, the phenol-surface interactions will be dominant. The adsorbed and free phenol molecular interactions are also involved in phenol

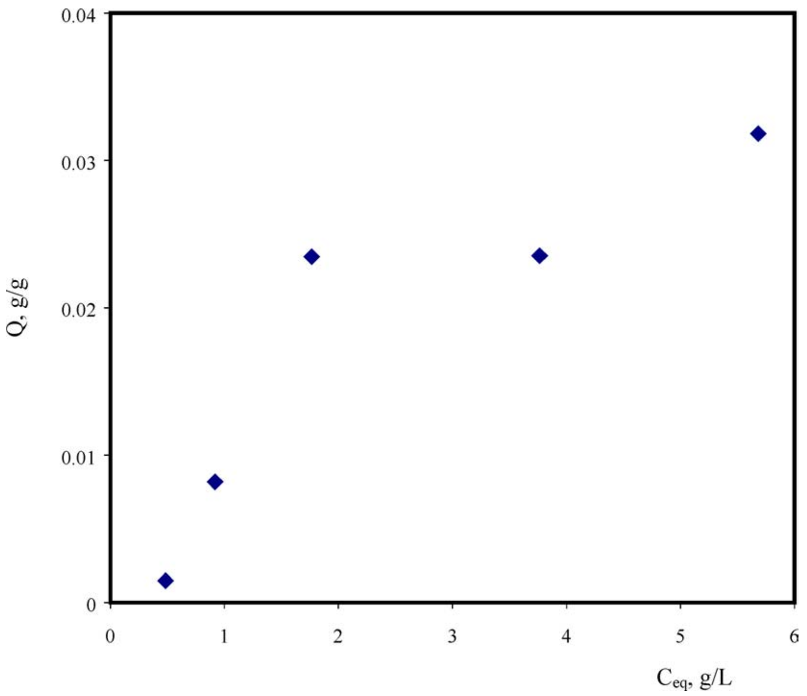


Figure 4. Adsorption isotherm of phenol on montmorillonite.

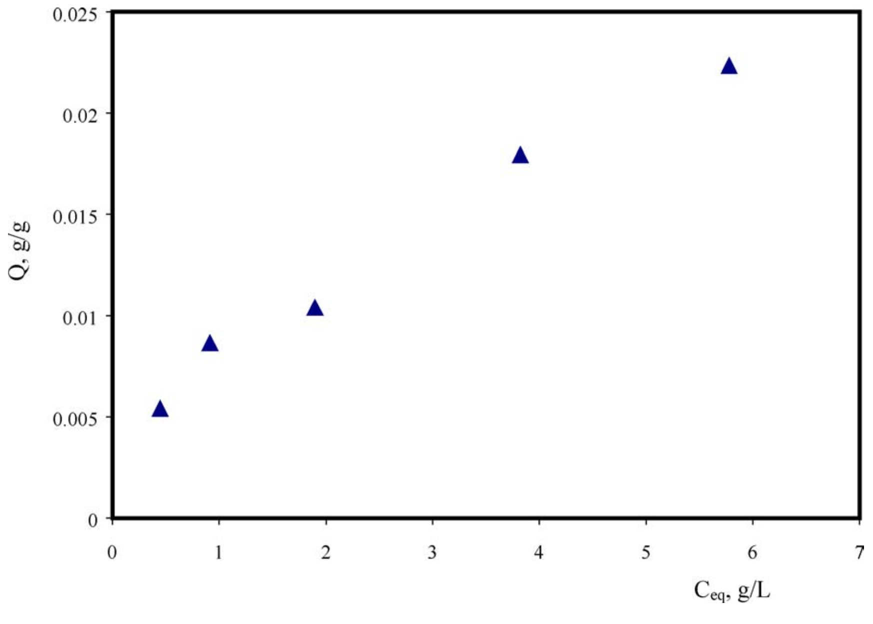


Figure 5. Adsorption isotherm of phenol on organo-clinoptilolite.

surface interactions by increasing the surface coverage and therefore the multilayer adsorption occurs. The shape of the isotherm confirms the multilayer adsorption.

Adsorption of Phenol on Modified Clinoptilolite

The exchange behavior of CTAB is given in Fig. 7. A close examination of the figure reveals that the

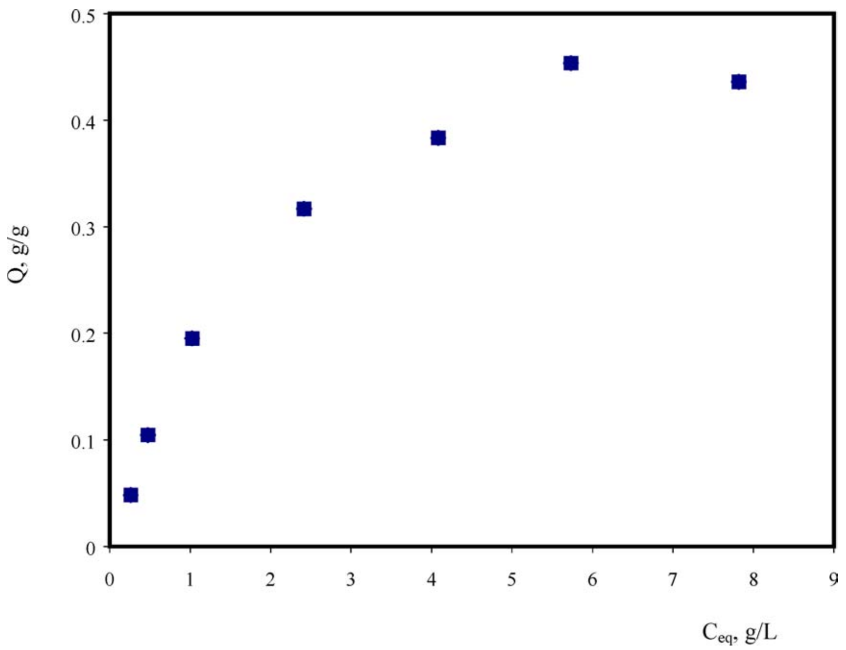


Figure 6. Adsorption isotherm of phenol on calcined hydrotalcite.

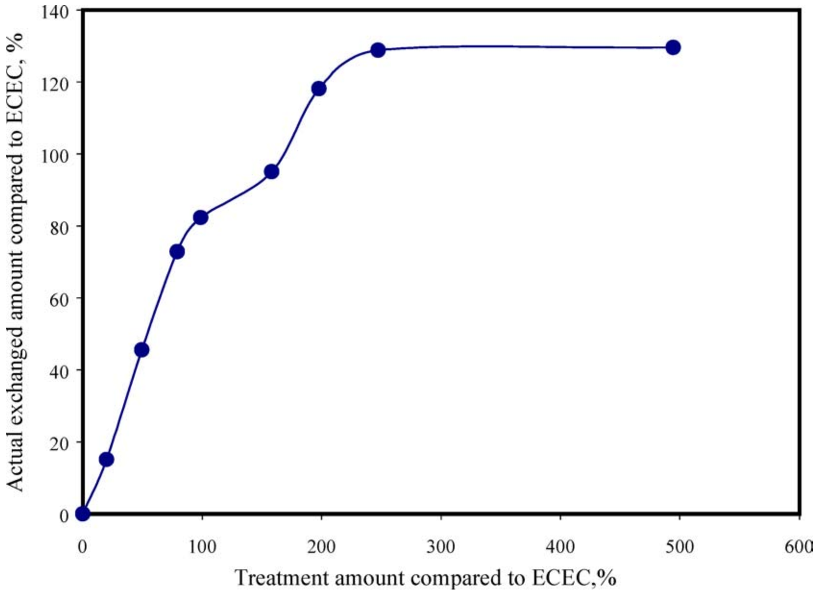


Figure 7. Exchange behavior of CTAB.

exchanged amounts are not in proportion to treatment amounts. A relatively fast increase is observed at low treatments and the exchange amount reaches 100% of ECEC for the treatments higher than 150% of ECEC. The amount exchanged corresponding to the amount of surfactant used in the preparation of organo-clinoptilolite is about 115% of ECEC.

Surfactant molecules are adsorbed on active sites on the external surface by leaving the voids between hydrocarbon chains oriented towards the solution phase. Even a part of the surfactant molecules adsorbed could be removed during the washing, as reported by Bowman et al. (1995), this amount will not be significant and thus a patchy surfactant bilayer causing positive charge on the surface of surfactant core will be formed. Thus, phenol is adsorbed probably via partitioning and anion exchange. Adsorption via partitioning is dominant in our work, because the ionic fraction of phenolate is 0.0016 and therefore most of the phenol is in a neutral molecular form at a pH of 7. Under these circumstances, the influence of interactions between phenol molecules and hydrocarbon chains is of importance. The slight increase in the last part of isotherm could be attributed to the variations in these interactions depending on saturation of the surfactant layer by phenol.

Adsorption of Phenol on Hydrotalcite

The pH values of suspensions containing 1 g of HTC and ionic fractions of phenolate are given in Table 5 as the function of time and initial bulk concentration.

Although hydrotalcite has positively charged surfaces and the amount of phenolate is rather high, adsorption of phenol on calcined hydrotalcite could not be considered as a simple anion exchange. As mentioned previously, calcined hydrotalcite is actually a magnesium aluminum oxide solid solution and this solution can be hydrated to reconstruct hydrotalcite when it is brought into contact with aqueous solutions containing anions. As shown in Table 5, pH values increase with time and this result agrees with that obtained by Hermosin et al. (1996). The increase in pH is due to the consumption of protons in the reconstruction of the layered structure. Since the amount of phenolate is high in the actual conditions, the phenolate will also participate in the reconstruction of HTC and therefore adsorption occurs during rehydration.

Adsorption Isotherm

In the three cases studied, the adsorbent and adsorbate interactions have an important impact on the adsorption behavior. The Freundlich equation was chosen for the modelling of adsorption behavior, since it contains a parameter, $1/n$, related to the affinity between the adsorbate and adsorbent. According to the conventional form of the equation, adsorbed amount seems to increase infinity in contrary to experimental observations. To correct this inconvenience, the equation is modified by replacing the reduced concentration with equilibrium concentration. The resulting equation is

$$Q = k'\left(\frac{C}{C_S}\right)^{\frac{1}{n}} \tag{1}$$

where k' is the limiting adsorbed amount at a saturated concentration (Urano et al., 1981). Modified Freundlich isotherms of phenol on montmorillonite, organo-clinoptilolite, and HTC are presented in Fig. 8. All isotherms fit fairly well in the to Modified Freundlich equation.

The parameters found following the least square routine and correlation coefficients are given in Table 6. The values given in Table 6 shows that HTC has the highest k' indicating the highest efficiency in the removal of phenol. The high n value found for clinoptilolite is attributed to electrostatic interactions promoted by the presence of a hydrocarbon layer on the clinoptilolite surface.

Table 5. Changes in pH of suspensions containing hydrotalcite and phenol.

Ci = 6 g/L				Before adsorption		After adsorption	
Time (h)	pH	ϕ*	Ci (g/L)	pH	ϕ	pH	ϕ
0	9.18	0.193	0.5	9.39	0.28	9.99	0.608
3	9.26	0.224	1.0	9.04	0.148	9.87	0.540
6	9.37	0.271	2.0	9.10	0.166	9.75	0.471
9	9.43	0.299	4.0	9.00	0.137	9.57	0.371
18	9.47	0.319	6.0	9.18	0.193	9.43	0.299
21	9.39	0.280					
24	9.43	0.299					

*ϕ Ionic fraction of phenolate.

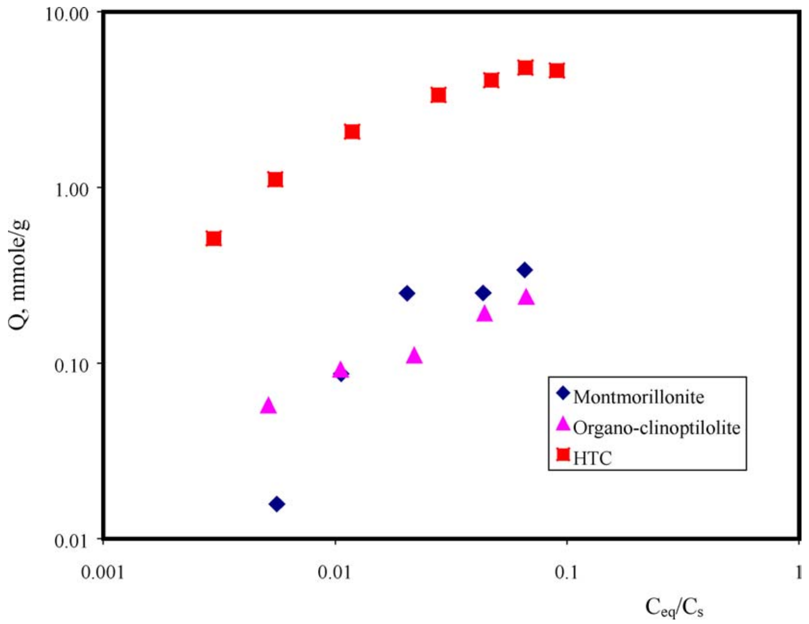


Figure 8. Reduced adsorption isotherms of adsorbents.

Adsorption Efficiencies

Percentages of phenol removed in the initial phenol concentrations are given in Fig. 9. A comparison of percentages removed reveals that the HTC is the most efficient one among the adsorbents used. It can adsorb 52% phenol while montmorillonite and organo-clinoptilolite can adsorb 12% and 11% phenol, respectively. The observations of the maximum in percent removals implies that the adsorbents will be used

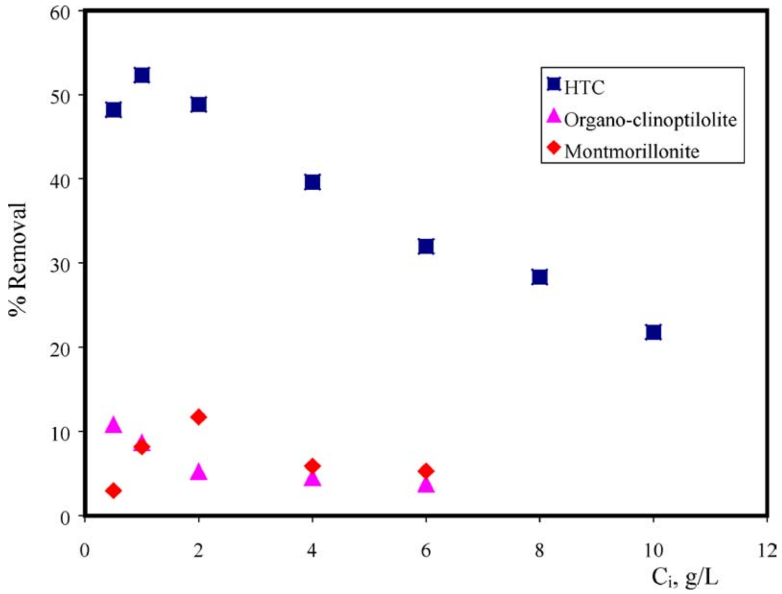


Figure 9. Adsorption efficiencies of adsorbents.

Table 6. Coefficients of the modified freundlich equation[a].

Adsorbent	k'	n	r
Montmorillonite	10.52	0.88	0.907
Organo-clinoptilolite	1.00	1.84	0.990
HTC	27.26	1.58	0.97

[a]The values of k' are shown as 10^3 times of the values in the unit of mole/g adsorbent.

more efficiently at the initial concentrations of 1 g/L for HTC, 2 g/L for montmorillonite, and 0.5 g/L for organo-clinoptilolite. Since the adsorption capacity of an adsorbent is mainly determined by surface saturation, the increase in the amount of adsorbent used yields in high percentages of phenol removal.

Conclusions

Phenol was adsorbed on;

> montmorillonite, in molecular form through the polarization of π-electrons. Since anion exchange sites of this adsorbent are very limited, adsorption of phenol in the form of phenolate, on the edges of montmorillonite is not comparable with that of phenol in molecular form.
>
> Modified-clinoptilolite, dominantly via partitioning mechanism, since most of phenol is in neutral molecular form at a pH of 7.
>
> CHT during rehydration where this adsorbent reconstructs HT by contact with an aqueous solution containing anions. So, adsorption of phenol on HTC could be considered as a location of phenolate anions formed at a pH of 9 in the interlayer region during the rehydration.

It has been concluded that;

> the adsorption behavior for all of the adsorbents studied in the removal of phenol could be explained by Modified Freundlich equation.
>
> The differences observed in the adsorption behavior were explained by the effect of the ionization behavior of phenol at pH values differing for each adsorbent as well as the different surface structures of each adsorbent.
>
> HTC was the best among the studied adsorbents since the amount adsorbed in the case of this adsorbent was considerably greater than those for the rest because of the sensible effect of the ionization behavior of phenol at high pH values and all mentioned structural properties of this adsorbent.
>
> Determination of the change in the % removal with the amount of adsorbent would be required in any evaluation of adsorbents.

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