The removal of phenolic compounds from aqueous solutions by organophilic bentonite

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Abstract

The adsorption of p-chlorophenol (p-CP) and p-nitrophenol (p-NP) on organophilic bentonite (dodecylammonium bentonite, DDAB) was studied as a function of solution concentration and temperature. The observed adsorption rates were found to be equal to the first-order kinetics. The rate constants were calculated for temperatures ranging between 25.0–35.0 °C at constant concentration. The adsorption energies, E and adsorption capacity, (q_m), for phenolic compounds adsorbed to organophilic bentonite were estimated by using the Dubinin-Radushkevic equation. Thermodynamic parameters from the adsorption isotherms of p-CP and p-NP on organophilic bentonite were determined. These isotherms were modeled according to Freundlich and Dubinin-Radushkevic adsorption isotherms and followed the V-shaped isotherm category with two steps. The amount of adsorption was found to be dependent on the relative energies of adsorbent–adsorbate, adsorbate–solvent and adsorbate–adsorbate interaction.
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1. Introduction

Clays are widely used as adsorbents due to their high specific surface area. However, their sorption capacitiy for hydrophlic (polar) organic molecules is very low due to the hydrophilic nature of the mineral surfaces. Natural clays possess a negative charge that is compensated by exchange cations, such as Na^+ and Ca^{2+}, on their surfaces. These exchangeable cations are strongly hydrated in the presence of water, resulting in a hydrophilic environment at the clay surface. The treatment of clays with inorganic or organic reagents increases the sorption capacity. There has been an increasing interest in the organic treatment of clays, i.e. organo-clays, whereby, the metal cations on the mineral surfaces are released in the case of change observed with the organic cations. The organic cations may also enter into ion-exchange reactions with exchangeable cations between the layers [1–3]. The surface of clay may be modified and become strongly organophilic. As a result, the organo-clay complex becomes an excellent sorbent for poorly water-soluble organic contaminants.

Removal of p-chlorophenol and p-nitrophenol from aqueous solution by activated carbon has been extensively studied [4–6]. Phenolic hydrocarbons including p-nitrophenol and p-chlorophenol are widely used in pharmaceutical, petrochemical and other chemical manufacturing processes. Due to the potential harm of phenolic compounds to human health and the environment, wastewater containing phenolic compounds must be treated before being discharged to receiving water bodies. Secondary biological treatment processes are commonly used for domestic and industrial wastewater, but they cannot treat phenolic wastewater at high concentrations, successfully. Therefore, new treatment technologies are still constantly researched and developed. Such technologies include biological degradation [7], chemical oxidation [8] and adsorption. Although many different adsorbents [9,10] have

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been utilized for removal p-nitrophenol and p-chlorophenol from wastewater, organo-clays have been used extensively as adsorbent for removal of phenol compounds [11,12].

For example, Zielke and Pinnvaia [13] studied modified clays for the adsorption of environmental toxicants, suggesting that the pillared, delaminated and hydroxy interlayered smectites for removal of toxic compounds. Mc.Bride.et al., [14] have shown that different kinds of clay-organic complexes possess varying adsorption properties for benzene, phenol and chlorobenzenes.

In link with these studies, the present study was carried out to investigate the sorption capacity of bentonite modified by dodecylammonium cation.

2. Material and methods

2.1. The preparation and characterization of the organophilic bentonite

The bentonite was used as clay in this study and obtained from the town of Reşadiye in Tokat (Turkey) [15]. The sample were characterised by X-ray diffraction, thermo gravimetric and FT-IR spectroscopic analyses. The chemical compositions of the sepiolite was found to be as follows; 58.3% SiO_2, 2.5% MgO, 16.0% Al_2O_3, 1.1% K_2O, 3.5% CaO, 0.6% TiO_2, 2.0% Na_2O, 0.1% P_2O_5, 3.1% ($FeO + Fe_2O_3$) and 13.0% loss on ignition. The IR spectrum of natural bentonite indicated a moderate Fe^{3+} content (885 cm^{-1}) with the presence of detectable quartz (697 cm^{-1}) and silica phase (797 cm^{-1}) impurities. The cation-exchange capacity (CEC) of the bentonite determined according to the ammonium acetate saturation method [16] was found to be 97 mmol per 100 g dry clay, The BET specific surface area was measured as 28 m^2/g. The hydrochloride salt solution of dodecylamine was prepared by mixing the appropriate amount of amine with 0.05 M HCl solution. The hydrogen ion concentration was approximately 20% in excess of the stoichiometric amount to assure complete conversion of the amine to the salt form.

The clay was dried at 110 °C for 24 h and then desiccated. Previously dried and desiccated sample was mixed with amine salt, the concentration of which was greater than the CEC of the clay. The mixture was subjected to mechanical shaking for 42 h at a constant temperature at 25 °C. The treated sample was separated from the mixture by centrifugation and washed several times with ethanol and ethanol–water (1:1) until free chloride was used up, dried at 40 °C for 24 h, and mechanically ground to 140 mesh. The surface area of the Dodecylammonium bentonite (DDAB) sample was determined by adsorption of N_2 at 77 K using B.E.T. method as 8 m^2/g. The clay sample was analysed by X-ray powder diffraction (XRD) using a Siemens D-500 diffractometer and CuKα radiation, The thermal analysis of sample was carried out at a heating rate of 10 °C/min. up to 800 °C using a shimadzu TGA-50 Thermogravimetric analyser, in the range of 10–800 °C and infrared (IR) spectroscopic (Maidac 1700 M

Model FT-IR) analyses before and after the modification process. The carbon content 11,4% of the adsorbents DDAB was analysed on a carlo Erba CHN Analyser and found [15].

2.2. The equilibrium sorption of single phenolics

The stock solutions were prepared in 10 mmol/dm³ $CaCl_2$ in order to promote the flocculation and to have a constant background electrolyte concentration. The adsorption isoterms were determined by using the batch equilibration technique. The kinetics and equilibrium adsorption of p-CP and p-NP were carried out by using the method aqueous solutions (p-CP and p-NP purity 99%). Of constant and various concentrations 20 ml p-CP and p-NP solutions were equilibrated with 0,1 g of adsorbent in 50 ml flaks with teflon caps. The suspension was shaken for 20 h at 25 °C, centrifuged and the supernatant analysed. The equilibrium concentrations of the phenolic compounds were calculated from the calibration curves, after measuring their absorbance values by using Perkin-Emler Lambda-2S model UV-VIS spectrophotometer at wavelengths of 279 nm and 258 nm, respectively. The solubility of p-CP and p-NP was determined as 27.0 and 5.3 g/dm3, and pK_a values are 9.18 and 7.15, respectively.

3. Result and discussion

3.1. Characterization of the DDAB

The XRD pattern of natural and DDA-treated bentonite was recoded and the basal spacings of 9.5 and 13.90 Å were observed. The expansion in the basal spacing of the bentonite due to the intercalation of DDAB was calculated as $\Delta d = d - 9.5$ Å, where d is the basal spacing of the DDA-treated clay and 9.5 Å is the thickness of a clay layer. Δd was found 4.4 Å. This obsevation suggests that DDA-ion molecules intercalate in to the interlayers of bentonite with a monolayer arragement. The surface area of the B and DDAB were determined as 28 and 8 m^2/g, respectively, by of the B.E.T. method.

3.2. The Freundlich, Dubinin-Radushkevic and Langmuir equations

The data obtained from the adsorption experiments carried out with p-CP and p-NP with concentrations between 1–0.1 mmol/dm³ and 0.5–0.04 mmol/dm³ were fitted with the Freundlich, Dubinin-Radushkevic and Langmuir isoterms. The folloving Freundlich equation was used to describe the equilibrium data [17].

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{1}$$

where K_F and n are characteristic constants. The single-solute sorption isoterms for p-CP and p-NP by organophilic bentonite at 25 °C are shown in Fig. 1a. and Fig. 1b.
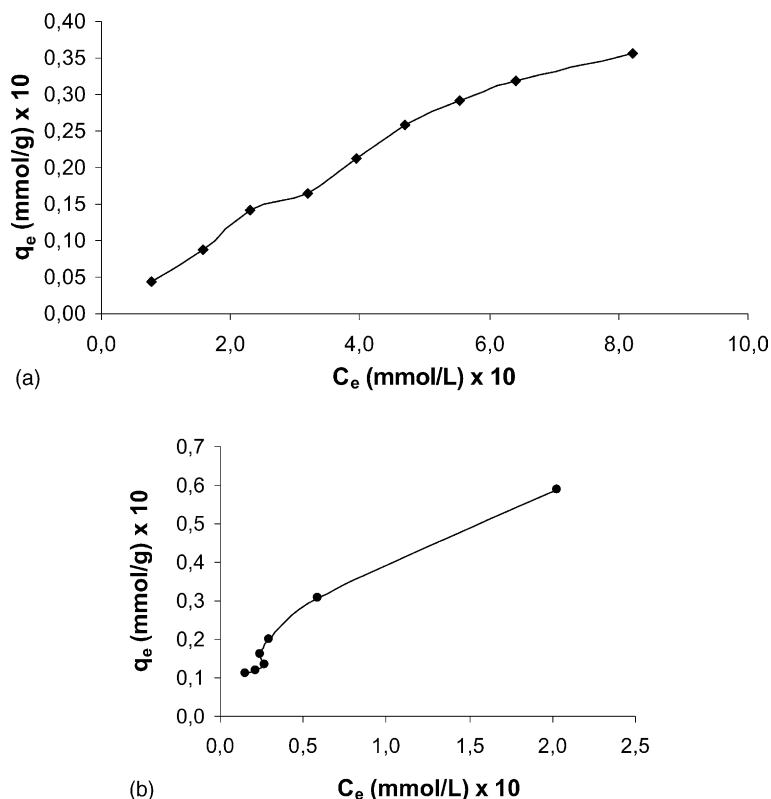
Fig. 1. (a) Equilibrium sorption isotherms for *p*-chlorophenol onto DDAB at 298 K and (b) equilibrium sorption isotherm for *p*-nitrophenol onto DDAB 298 K.

The regression equations at 298 K along with the constants K_F, n and the correlation coefficient R^2 are listed in Table 1.

Langmuir equation was used to describe the equilibrium data [18].

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{b}{K_L}\right) C_e \tag{2}$$

where C_e is the equilibrium solution concentration, q_e is the amount of *p*-CP and *p*-NP adsorbed at the equilibrium, constant K_L and b are the characteristics of Langmuir equation. Therefore, a plot of C_e/q_e versus C_e gives a straight line with slope b/K_L and intercept $1/K_L$. K_L is Langmuir equilibrium constant and the ratio b/K_L gives the theoretical monolayer saturation capacity, q_m. Parameters are listed Table 2.

The DR isotherm is more common than the Langmuir isotherm, because it does not assume a homogenous surface

or constant sorption potential [19,20]. The DR equation is,

$$q_e = q_m \exp(-\beta \varepsilon^2) \tag{3}$$

where q_e is the amount of *p*-CP and *p*-NP adsorbed at equilibrium, β is a constant related to the adsorption energy, q_m is the theoretical saturation capacity, ε is the Polanyi potential, which is equal to RT exp $(1/C_e)$. The lineer form of Eq. (3) is,F

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{4}$$

The slope of the plot of $\ln q_e$ versus ε^2 gives β (mol^2/kj^2) and of the intercept yields the sorption capacity, q_m (mol/g). The DR parameters are listed in Table 1. According to following equation [20], we can obtain the sorption free energy (Fig. 2).

$$E = (2\beta)^{-1/2} \tag{5}$$

The magnitude of E is useful for estimating the type of adsorption procces.

Table 1

Parameters obtained from Freundlich, Langmuir and Dubinin-Radushkevic equations

Phenolics	Freundlich			Dubinin-Radushkevic				Langmuir		
	n	K_F (mol/g)	R^2	q_m (mmol/kg)	β (mol^2/kj^2)	E (kj/mol)	R^2	K_L (dm^3/g)	b (dm^3/g)	R^2
p-CP	1.10	0.025	0.99	629.24	9×10^{-3}	−7.454	0.99	0.060	0.34	0.72
p-NP	1.48	0.020	0.95	771.10	5.7×10^{-3}	−9.363	0.99	0.641	4.60	0.29

K_F and n are Freundlich constant, q_m is ultimate capacity per unit area clay, β is a related to sorption energy, E is sorption energy, R^2 is coefficient of correlation, the constant K_L and b are characteristic of the Langmuir equation.

Table 2
Kinetic and thermodynamic parameters

Phenolics	Temperature (K)	K_{ads} (min)$^{-1}$	K_d	$\Delta G°$ (kj/mol)	$\Delta H°$ (kj/mol)	$\Delta S°$ (kj/molK)
p-CP	298	1.17×10^{-2}	2.72	−2.479	−36.906	0.096
	308	2.80×10^{-2}	2.62	−2.466		
p-NP	298	1.10×10^{-2}	14.65	−6.651		
	308	1.57×10^{-2}	15.45	−7.010	−46.276	0.787

K_{ads} is the adsorption rate constant, K_d is disrubuted coefficient, $\Delta G°$ is Gibbs free energy, $\Delta H°$ isostheric adsorption heats and $\Delta S°$ is entropy.

As shown in Table 1, data correlated with Freundlich and DR equations are used to interpret the results. The constant n in Freundlich isotherms is larger for p-NP than that of p-CP. Among two phenolic compounds tested, p-NP is the most hydrophobic, having the highest adsorption capacities on adsorbent.

A supplemented donor–acceptor adduct mechanism might be involved in the p-NP adsorption on clay-based adsorbent. According to Lewis acid–base theory, the modified clays including metal cations can be considered as lewis acides, while phenolic compounds in aqueous solution can be regarded as lewis bases and bronsted acids. The adsorption capacity of p-nitrophenol is abnormally high considering its hidrophobicity. Therefore, the sorption energy E of p-NP is higher than that of the p-CP.

3.3. Sorption kinetics of single phenolics

The rate of phenolic compounds adsorption by DDAB 298 and 308 K tends to follow the Lagergren's first-order rate equation [21].

$$\ln(q_e - q_t) = \ln q_e - K_{ads} t \qquad (6)$$

where q_t is the amount of phenolic adsorbates adsorbed at time t, q_e is the amount of phenolic adsorbates adsorbed at the equilibrium, K_{ads} is the adsorption rate constant. K_{ads} values were obtained in the lineer plots. The adsorption rate constants were determined from the slopes of the plots. The sorption is rapid during the first 30 min and the equilibrium is then attained within 120 min. K_{ads} constant for p-CP and p-NP sorption on organophilic bentonite were determined at 298 K and 308 K, respectively, as in Table 2.
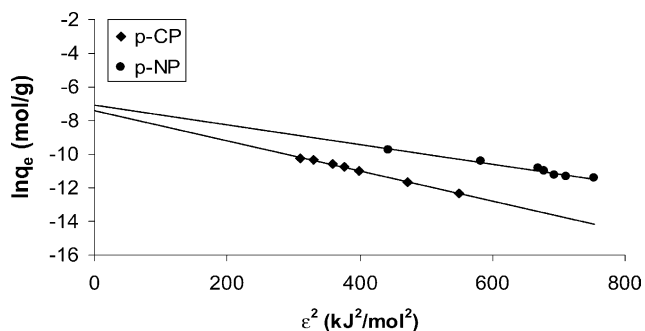

Fig. 2. The DR sorption isotherms for p-chlorophenol and p-nitrophenol onto DDAB at 298 K.

3.4. Thermodynamic parameters

The amounts of sorption of single-solute phenolics by DDAB clay were measured in a temperature 298–308 K. The equilibrium partition constant K_d was calculated as follows,

$$K_d = \frac{q_e}{C_e} \cdot V \qquad (7)$$

A plot of $\ln K_d$ versus $1/T$ gives a straight line. The following relationships have been used to evaluate the thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$.

$$\Delta G° = -RT \ \ln K_d \qquad (8)$$

$$\ln K_d = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \qquad (9)$$

The slope of the plot gives the value of $\Delta H°$, while the intercept yields the value of $\Delta S°$. The change in free energy was calculated at 298 and 308 K from Eq. (8), and the calculated values of isosteric adsorption enthalpies, entropies and free energies of phenolic compounds on DDAB are presented in Table 2. At low C_e, the interaction between adsorbate and adssorbent is seen, therefore, the direct interaction between solute and adsorbent and the formation of donor–acceptor adducts can explain the high adsorption enthalpy change of p-nitrophenol. In addition the increase of the interaction between adsorbate–adsorbent, is also seen the interaction between solute in solution and solute adsorbed on sorbent gradually. Therefore, the adsorption capacity increases by degrees. Since p-nitrophenol adsorbed on adsorbent can form the stronger hydrogen bonding than the p-chlorophenol [22]. Thus, it has higher isosteric adsorption enthalpy.

4. Conclusion

This paper deals with, the removal of two phenolic compounds in aqueous solution by DDAB. The two phenolic compounds were present predominately in their molecular form. The DDAB prefer, p-NP relative to p-CP, due to the fact that the main interaction between p-NP and DDAB is consistent with donor–acceptor and hydrogen bonding. The adsorption isotherms of the phenolic compounds on organophilic bentonite were fitted to the Freundlich and Dubinin-Radushkevic equations.

The p-nitrophenol gave a type V isotherm in classification of Gregg and Sing [11], which was characterized by an initial convexity followed by a slight plateau and then the beginning

of a final upsweep. The *p*-chlorophenol isotherm also exhibited type V characteristics, but lacked the final upsweep. Such isotherms are characteristics of weak adsorbate-adsorbent interaction.

The values of the isosteric enthalpy are indicative on exothermic procces and their magnitude < 43 kj/mol manifest the adsorption of two phenolic compounds on the organophilic bentonite to be a procces of physical adsorption. The results obtained from this study were compared to the published data in the same field. Our findings are in agreement with most of them. The Dubinin-Radushkevic isotherm was demonstrated to provide the best correlation for the sorption of the phenolic compounds on organophilic bentonite.

Acknowledgement

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