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Removal of Phenol from Aqueous Solution by Activated Clay

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Activated clay has been employed to remove phenolic compounds, a common contaminant in wastewaters, being generated from petroleum and petrochemicals, coal conversion and phenol-producing industries. Because of its high surface area per unit area, activated carbon is the most effective adsorbent and exhibits high capacity for adsorption of phenolic compounds. Kinetics and isotherm studies were conducted to evaluate the adsorption capacity of natural and activated clay. The effect of contact time, pH, initial adsorbate concentration and temperature were studied. In comparison between the capacity adsorption of natural and activated clay, it has been seen that the activated clay adsorbs more than natural clay.

Key Words: Adsorption, Clay, Isotherm, Phenol.

INTRODUCTION

Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health. Stringent US Environmental Protection Agency[1, 2] (EPA) regulations call for lowering phenol contents in wastewater to less than 1 mg/L. To be eliminated, the phenol must be oxidized, however, the oxidation processes have been described in a great number of works[3–5]. Beside of these methods[6], activated carbons are among the most effective adsorbents, having high surface area per unit mass. Activated carbon exhibits high adsorption capacity for phenolic compounds[7–11]. Due to the relatively high cost of activated carbons, there have been attempts to utilize natural adsorbents to remove organic and inorganic contaminants from wastewaters. In recent years, clay and mineral clays were utilized to remove many of the pollutants from wastewaters, because of their abundance in most countries and their low cost. The adsorption of phenol on natural bentonite was also studied[6, 12–15].

The aim of this work is to investigate, experimentally, the potential of natural and activated clay to adsorb phenolic pollutants using phenol as a model component. A complete kinetic study was conducted to evaluate the adsorption capacity of activated clay and compared it with natural clay.

EXPERIMENTAL

The natural clay used for acid activation was from Algerian Society ENOF.

Natural clay (25 g) used was agitated with 500 mL of 1 M sulphuric acid at 98°C for 6 h; then the mixture crude was cooled, filtered and washed several times to eliminate chloride and sulphate ions and finally dried at 120°C oven for a few hours. The analytical results of the acid activated clay are given in Table-1.

Table-2 summarizes the methods and instruments used for the analysis of activated clays.

TABLE-1
CHARACTERISTICS OF ACTIVATED CLAY

Parameter	Value
Colour	White
pH	3.42
Density	2.32 g/mL
Colloidality	15.5%
CEC	40 meq/100 g of clay (test of methylene blue) 39 meq/100 g of clay (conductimeter method)
Specific surface constitution	171.5928 m^2/g; montmorillonite, kaolinite and illite
Chemical composition	1.00% Fe_2O_3; 2.00% K_2O; 0.05% TiO_2; 0.07% CaO; 48.00% SiO_2; 0.10% Na_2O; 0.3% MgO; 37.00% Al_2O_3 and 12.10% L.O.F.

TABLE-2
METHODS USED FOR ANALYSIS

Parameter marks	Used method	Utilized device
Specific area	BET method	Micrometrics GEMINI VACPREP 061
Constitution	X-rays diffraction	Ganiometer Philips of PW3710 type (radiation kα of copper, $\lambda = 1.54056$ Å)
Chemical composition	Fluorescence-RX	F.R.X. of type P.W.1404X-ray spectrometer

Batch adsorption test

Batch adsorption experiments were carried out by allowing an accurately weighed amount of activated clay to reach equilibrium with phenol solutions of known concentrations. Different weights (2 to 35 mg) of clay were added to narrow-neck bottles each containing 50 mL of solution. The bottles were shaken in a temperature-controlled water bath shaker (B. Braun, model Infors AG, Bottmingen, Gremany). The temperature was fixed at 20°C. The narrow-neck bottles were shaken fastly for 15 min, then slowly for another 15 min. At the end of the equilibrium period, the contents of the bottles were filtered, centrifuged for half an hour and the supernatant was subsequently analyzed for residual concentration of phenol.

RESULTS AND DISCUSSION

Effect of pH: The adsorption of phenol by natural clay was studied at various pH values. Different amounts of clay (2–35 mg) were added to several bottles containing 50 mL of phenol solutions (5.5 ppm). The pH of the solutions was adjusted to values of 2, 4 and 10, by adding 0.1 N HCl or 0.1 N NaOH solution.

As shown in Fig. 1 that the adsorbed amount of phenol decreases with increasing pH values. This can be attributed to the dependency of phenol ionization on the pH value. Effectively, phenol is a weak acid (pKa = 10); it will be adsorbed to a lesser extent at higher pH values due to the repulsive forces of phenolate ions formed[12].

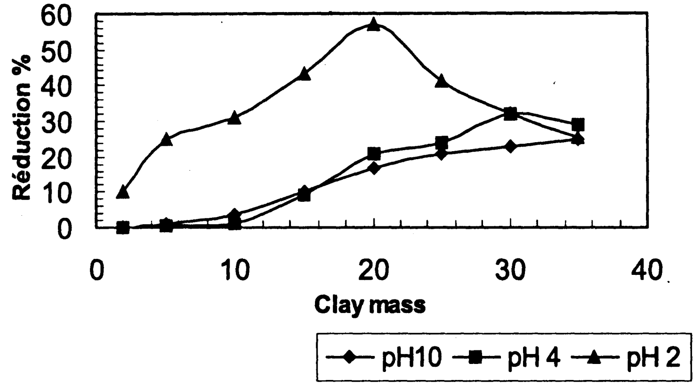

Fig. 1. Relationships between phenol concentration and amounts of clay at different pH

Mass clay effect: To different bottles each containing 50 mL phenol solution at concentration of 5.5 ppm, were added various clay masses and put under agitation during 30 min. The stirring velocity was 250 rd/min. The filtrates were analyzed by UV spectroscopy.

The results (Fig. 2) show that the maximum of phenol adsorption (52%) is obtained with 15 mg of activated clay. As the amount exceeds 15 mg, its capacity of

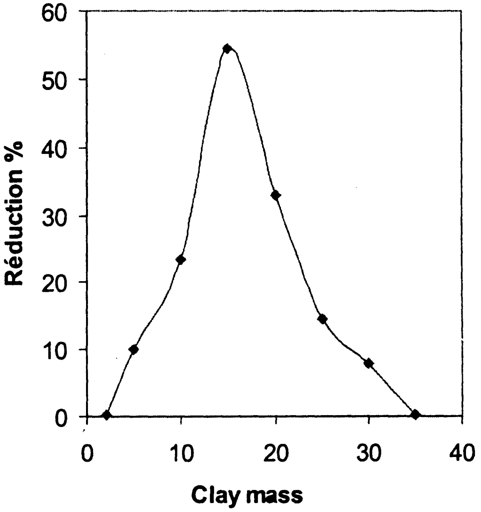

Fig. 2. Relationship between per cent of phenol adsorbed and amount of activated clay

adsorption decreases, which may be attributed to the presence of repulsive forces (negative charges at surface clay) related to the high clay concentration.

Time contact: 50 mL of phenol solution (5.5 ppm), 15 mg of activated clay was put under agitation for 180 min. Then, every 10 min, a volume of filtrate was analyzed by UV. At the same time the pH and conductivity of the filtrate were measured.

The results (Fig. 3) show that the equilibrium time required for adsorption of phenol on activated clay is almost at 20 min. These results also indicate that the sorption process can be considered fast because of the large amount of phenol attached to sorbent within the first 20 min.

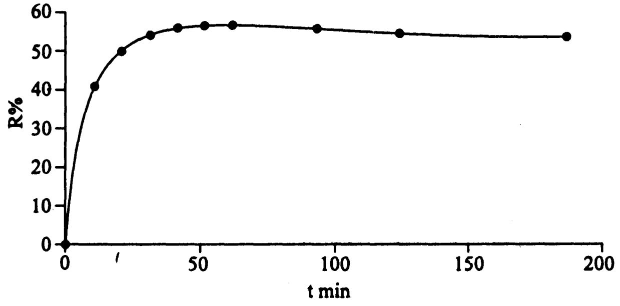

Fig. 3. Plot of per cent of phenol adsorbed versus time of contact

Fig. 4 indicates that the conductivity increases with increase of the amount of adsorbed phenol and at the same time the pH remains practically constant, which could be explained by an exchange phenomenon between metal cations present in activated clay and protonated phenol.

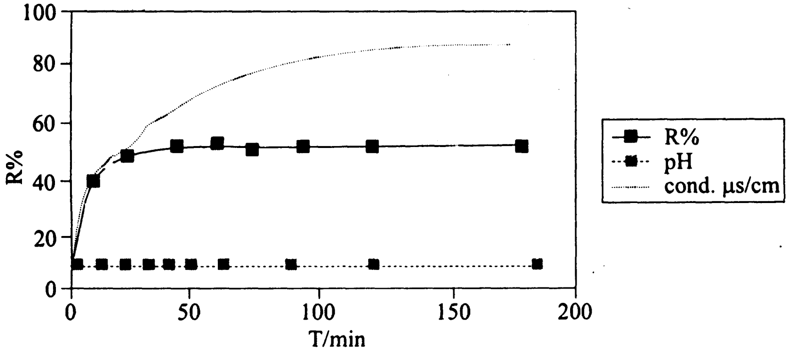

Fig. 4. Variation of per cent phenol adsorbed, pH and conductivity versus to time contact

Adsorption isotherm

To different solutions at various initial concentrations (C_i) were added 15 mg portions of activated clay and shaken for 30 min. When equilibrium was reached, the filtrate was analyzed by UV spectroscopy. The results obtained are regrouped in Table-3.

TABLE-3
RELATIONSHIP BETWEEN EQUILIBRIUM PHENOL CONCENTRATION AND ITS ADSORPTION BY ACTIVATED CLAY AT VARIOUS INITIAL PHENOL CONCENTRATION VALUES

C_i (mg/L)	C_e (mg/L)	x/m (mg/g)	C_e/x/m	log x/m	log C_e
1	0.36	2.13	0.16901408	0.32837960	–0.4436975
5	2.31	8.96	0.25781250	0.95230801	0.36361198
10	4.32	18.93	0.22820919	1.27715061	0.63548375
25	18.57	21.43	0.86654223	1.33102217	1.26881190
35	25.33	32.23	0.78591374	1.50826031	1.40363519

C_e: concentration at equilibrium of phenol in liquid phase mg/L,
x/m: amount of phenol in the solid phase mg/g.

The plot of x/m *vs.* the equilibrium concentration (Fig. 5) shows an S model of Langmuir. It indicates a vertical adsorption of the polar mono-functional molecules on a polar adsorbent. On the other hand, these results show that the adsorption of phenol by activated clay increases as the initial concentration increases. So increasing the initial phenol concentration would increase the mass transfer driving force and therefore the rate at which phenol molecules pass from the bulk solution to the particle surface.

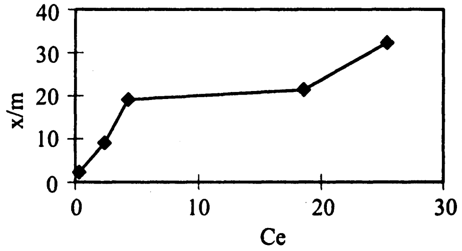

Fig. 5. Isotherm of phenol adsorption

Comparison between the two adsorption models, Langmuir and Freundlich

The following relation can represent the linear form of Langmuir isotherm model:

$$\frac{C_e}{x/m} = \frac{1}{Q_0 B} + \frac{C_e}{Q_0}$$

where Q_0 (mg/L) and B (L/mg) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption. These constants can be evaluated from the intercept and the slope of linear plot of experimental data of C_e/x/m *vs.* C_e (Table-4).

TABLE-4
PARAMETERS OF ADSORPTION ISOTHERM FOR THE LANGMUIR AND FREUNDLICH MODELS

Models	Langmuir			Freundlich		
Parameters	R^2	B	Qo (mg/g)	R^2	N	K
Values	0.90	0.169	34.84	0.92	1.67	4.93

R^2 values, which are measured goodness-of-fit (Table-4), show that both Langmuir and Freundlich isotherm can adequately describe the adsorption data

Effect of temperature

Different solutions of phenol with various concentrations (100 mL) mixed to the same amount of activated clay (30 mg) were shaken for 30 min at different temperatures. At equilibrium time the filtrate was analyzed in each case.

TABLE-5
COEFFICIENT OF PARTITION K_d AND RATE OF PHENOL ELIMINATION ACCORDING TO THE TEMPERATURE

Temperature Concentration of phenol (mg/L)		30°C	40°C	50°C
10	C_e (mg/L)	3.99	4.26	5.3
	Reduction (%)	60.1	57.4	47
	K_d (cm^3/g)	5020.88	4491.39	2955.97
	ln K_d	8.52	8.40	7.99
20	C_e (mg/L)	7.08	9.35	11.2
	Reduction (%)	64.6	53.25	44
	K_d cm^3/g	6082.86	3796.79	2619.04
	ln K_d	8.71	8.49	7.87
50	C_e (mg/L)	28.7	9.45	30.26
	Reduction (%)	42.6	41.1	39.48
	K_d (cm^3/g)	2473.86	2325.97	2174.48
	ln K_d	7.81	7.75	7.68

The results (Table-6) show that the partition coefficient decreases when the temperature increases and it decreases at a fixed temperature when the initial phenol concentration increases. While the constant decreases with the increase in temperature, the relation of Arrhenius shows that the constant speed varies exponentially with the temperature as below:

$$k = k_0 e^{-E_a/RT}$$

Thus when K decreases, E_a increases.

The relation of Van't Hoff is as follows:

$$\Delta G = -RT \ln K_d$$

The results obtained in Table-6 for the values of ln K_d, show that $\Delta G < 0$. This proves that it has spontaneity in the process of adsorption. The enthalpy ΔH is positive, so the mechanism is exothermic. Moreover, it may be predicted that the phenol is eliminated by ion exchange phenomenon[14].

Conclusion

Natural clay capability of phenol adsorption from aqueous solution depends on the medium pH. A low pH favours the adsorption but the amount of phenol adsorbed does not reach 29%. To increase its capacity of adsorption, the natural clay was treated with sulphuric acid. The specific surface increased and its acid character was reinforced. Its capacity of adsorption increased, because the adsorption was very fast and 65% of phenol was removed from aqueous solution ($C_i = 35$ mg/L). This adsorption was greatly affected by the initial phenol concentration. The temperature has not an important effect on the equilibrium of elimination phenol. Futher, the reaction is exothermic and could be considered as ion exchange. The Langmuir and Freundlich isotherms were found to be applicable for adsorption equilibrium data. The activated clay could be utilized in treatment of industrial wastewater.

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