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Kinetic Study on Removal of Phenol from Water by Organo-Bentonite

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By a simple ion exchange process, Na^+ in the bentonite structure can be replaced by cationic detergent molecules and produce organo-bentonite. By this process the surface properties of bentonite can be modified and the produced organo-bentonite can be used for removal of organic contaminants from water. In this study bentonite was treated with alkyldimethylbenzyl ammonium chloride (ADBAC). In sorption experiments, each batch test sample was prepared with 0.1, 0.5 and 1.0 g bentonite (B) and modified bentonite (MB) separately together with aqueous phenol solution. Adsorption of 10 and 50 mgL^{-1} phenol on to bentonite and modified bentonite were investigated separately. Batch kinetic and isotherm studies were carried out to evaluate the effect of contact time, initial concentration and pH. Removal of 10-100 mg L^{-1} phenol, by 10 gL^{-1} ordinary bentonite was 10-20 % whereas in the same condition removal by synthesized organo-bentonite, was 60-80 %. Adsorption was reached in equilibrium within 3 and 6 h for organo bentonite and bentonite, respectively. Adsorption kinetics obeys a first order reaction. Adsorption isotherms were fitted with Langmuir and Freundlich models. Corresponding constants of both models were calculated. Adsorption efficiencies were slightly increased with increasing the sorbents dose. Optimum pH for using synthesized sorbent was 7. The bentonite may function as a recyclable surfactant support for the adsorption and subsequent combustion of organic pollutants.

Key Words: Low cost sorbent, Organo-bentonite, Phenol, Adsorption.

INTRODUCTION

Adsorption is a process to remove pollutants from water and wastewater. There are different adsorbents, some of them such as activated carbon is effective, but its initial cost is high and needs costly regeneration process[1]. Many researchers focused their studies to find cheaper and effective sorbents. Adsorptive properties, effectiveness and cost are the main criteria for choosing an alternative sorbent. Numerous researchers have studied adsorption properties of materials such as montmorillonite, clinoptilolite, hydrotalcite, smectite, peat, clay soil and bentonite[2-6].

Bentonite is one type of clays mainly composed of montmorillonite which is a 2:1 type aluminosilicate. In the crystalline structure of bentonite there is an alumina octahedral layer between two tetrahedral layers of silica. There are exchangeable cations such as Ca^{2+} or Na^+ to compensate the negative charges, bentonite has capacity to exchange these cations with cationic surfactants[7]. This property can be used to chemically modify of bentonite. Replacement of this ions with quaternary ammonium cations of the general form $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR']^+$, where R is a large alkyl hydrocarbon, yields organo-clays with organophilic characteristics[8]. Some researchers have studied adsorptive properties of organo-clays to remove phenols from water and wastewater[9-15]. Organo-clay was studied for organic contaminants removal from wastewater[16]. In the last decade there was many interest to investigate adsorptive characteristics of organo-clay to remove organic pollutants from wastewater[17-28]. But all of the researchers used high concentration and analytical grade of cationic detergent, pretreated bentonite by different steps and a lot of distilled water for washing the synthesized organo-bentonite. This caused the increase in the price of sorbent. In commercial scale, production of effective and low cost sorbent is important.

The present study is undertaken to synthesize low cost organo-bentonite and to determine the effect of contact time, sorbate and sorbent dose and pH on adsorption capacity of synthesized low cost organo-bentonite for phenol removal from aqueous solution.

EXPERIMENTAL

Bentonite used in this study was natural bentonite from Yazd, Iran. Characteristics of the bentonite was as follows: SiO_2:68.259 %, Al_2O_3:11.436 %, Na_2O:10.830 %, Li_2O:2.859 %, Fe_2O_3:2.801 %, K_2O:0.487 %, CaO:0.406 %, cationic detergent used to synthesis of organo-bentonite was common disinfectant, alkyldimethylbenzyl ammonium chlorides (ADBAC), (commercial benzalkonium chloride) produced in Iran. Aqueous detergent solution with concentration of 50 % v/w was prepared. Phenol was analytical grade from Merck Company.

Preliminary treatment of bentonite: A total of 100 g bentonite was washed twice with enough distilled water and placed in Imhoff cones for wet sedimentation (for discarding impurities). The slurry of bentonite was contacted with 0.1 M NaCl solution for 24 h on a shaker in order to preparation of Na-bentonite. Then the suspension was filtered through a Buchner funnel and the filtration cake was rinsed twice with enough distilled water and dried at 105 ºC in the oven.

Preparation of organically modified bentonite: A total of 50 g of previously Na-bentonite powder was added to 500 mL of cationic detergent (ADBAC 40 % vol.). The mixtures was agitated on a rotary shaker for 24 h at room temperature. The ADBAC-bentonite suspention was then washed with distilled water repeatedly. Rinsing was repeated until the filtrate was chloride free (tested with 0.1 M $AgNO_3$). The organo-bentonite was dried at room temperature and stored in bottles for experimental use.

Sorption experiments: Batch adsorption experiments were carried out by allowing an accurately weighed amount of natural and organo-bentonite separately to reach equilibrium with phenol solutions of known con centrations. Initial concentrations of phenol were 10, 20, 50 and 100 mgL^{-1}. Preliminary kinetic experiments showed that adsorption equilibrium for synthesized organo-bentonite and natural bentonite were reached within 3 and 6 h, respectively. However, for subsequent experiments, the samples were left for 24 h to ensure equilibrium. Known weight of sorbents, 0.5 g of synthesized organo-bentonite and ordinary bentonite were added to series of bottles containing 50 mL phenol solution separately. The bottles were subsequently capped by screw Teflon caps and shaken on a shaker in a dark place to prevent photo-oxidation. Removal of phenol by bentonite and organo-bentonite was studied at acidic and alkaline solutions. The pH was adjusted using dilute HCl or NaOH solutions. Three concentrations of phenol (10, 50 and 100 mg L^{-1}) were prepared and adjusted to pH values of 3 and 10 by acid and alkaline solution and contacted with 10 g/L of bentonite and organo-bentonite during 12 h.

At the end of each contact time, the contents of the bottles were centrifuged for 20 min at 4000 rpm and then supernatant was subsequently analyzed for residual concentration of phenol. The concentration of phenol was determined following the method of Gales and Booth (1975) which is based on spectrophotometric analysis of the developed color resulting from the reaction of phenol with 4-aminoantipyrine, which were determined spectrophotometrically using a Jasco-7800 (Japan) UV-vis. spectrophotometer. The amount adsorbed was determined from differences in the initial and final concentration of phenol. All experiments were carried out at least two times and average to ensure reproducibility.

Photograph of experimental setup

RESULTS AND DISCUSSION

Effect of contact time: The adsorption data for the removal of phenol by 10 g L^{-1} organo-bentonite and ordinary bentonite *versus* contact time at different initial concentrations are presented in Figs. 1 and 2. Adsorption of phenol was rapid in the first hour and followed by a slower rate and finally approached to equilibrium. The equilibrium time for organo-bentonite and bentonite was 3 and 6 h, respectively. The rate of phenol uptake and adsorption capacity of organo-bentonite was higher compared to bentonite. These results also indicate that adsorption of phenol by organo-bentonite is greater and faster than bentonite because of the largest amount of phenol attached to the organo-bentonite within the same time of contact. It was also seen that an increase in initial phenol concentration results in increased phenol adsorbed.

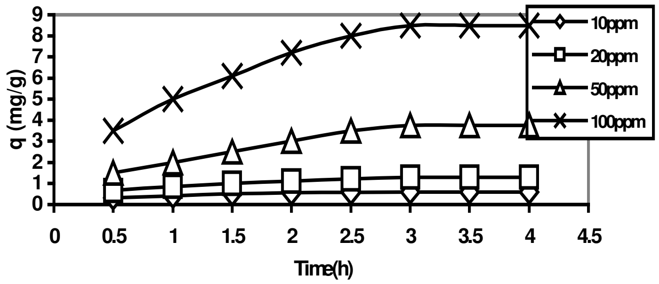

Fig. 1. Effect of contact time on adsorption of phenol by organo-bentonite (10 g/L)

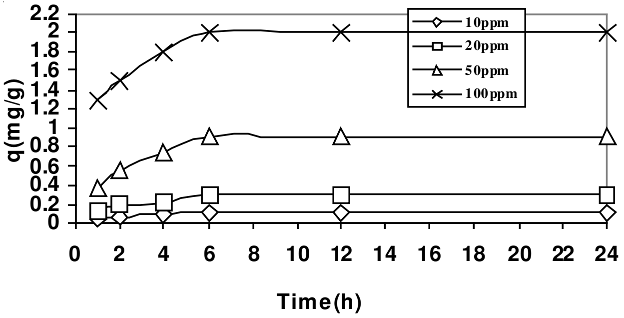

Fig. 2. Adsorption of phenol by ordinary bentonite (10 g/L) at different contact time

Effect of phenol concentration: Effect of initial phenol concentration on percentage of removal by bentonite and organo-bentonite is shown in Fig. 3. There is a great difference in removal efficiency between two sorbents. Removal efficiency of 10-100 ppm phenol by synthesized organo-bentonite was 60-80 % whereas by bentonite was around 10-20 %. Adsorption of phenol by bentonite and organo-bentonite slightly increases as the concentration of phenol increased. As it can be seen from Fig. 3, synthesized organo-bentonite can remove phenol 4 to 6 times greater than ordinary bentonite.

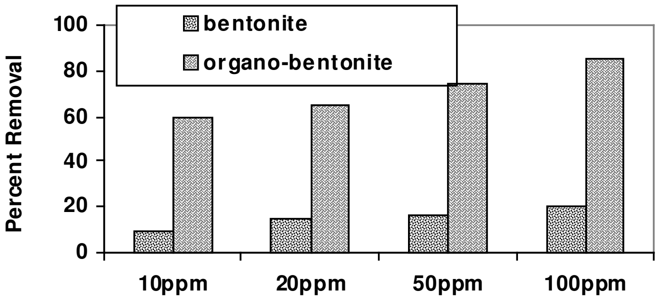

Fig. 3. Removal of phenol in different concentration by 10 g/L of bentonite and organo-bentonite at pH = 7

By increasing the phenol concentration, the mass transfer driving force will increase and therefore many molecules of phenol transfer from the bulk solution to the diffuse layer.

Effect of pH: Bentonite and organo-bentonite were contacted with phenol in acid and alkaline solutions separately. Results are displayed in Fig. 4. As it can be seen from Figs. 3 and 4, the optimum pH for phenol removal by organo-bentonite is natural condition (pH = 7), the percentage of phenol removal is in the range of 60-85 %. Phenol removal by bentonite and organo-bentonite in the acidic condition is greater than alkaline condition.

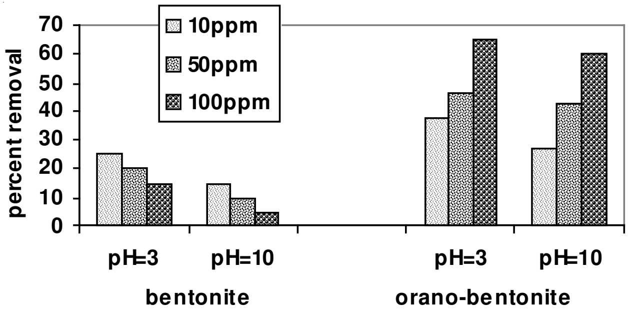

Fig. 4. Effect of pH on adsorption of phenol by bentonite and organo-bentonite

The adsorbed amount of phenol decreases with increasing the pH. This can be attributed to the dependency of phenol ionization on the pH. The ionic fraction of phenolate ion can be calculated from: $\text{Phenolate}_{\text{ions}} = [1 + 10^{(\text{pKa - pH})}]^{-1}$. Phenolate ion increases with increasing the pH. Phenol is a weak acid ($pK_a = 10$) and will be adsorbed to a lesser extent at higher pH values due to the repulsive forces prevailing at higher pH values. Similar behaviour has been reported by Banat *et al.*[5] for the removal of phenol by bentonite.

Adsorption isotherms: The adsorption of phenol on the bentonite corresponds to the S-type isotherm in Giles classification, suggesting that the adsorbate-adsorbate interaction is stronger than the adsorbate-adsorbent interaction. Several models have been published in the literature to describe experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration in solutions at different pH values. The linear form of the Langmuir isotherm model can be represented by the following relation:

$$1/q_e = 1/Q^o + (1/bQ^o)(1/C_e)$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L) and Q^o (mg/g) and b (1/mg) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and the slope of the linear plot of experimental data of 1/q, *versus* $1/C_e$. The linear form of the Freundlich isotherm model is given by the following equation:

$$\ln q_e = \ln K_F + 1/n \ln C_e$$

where K_F and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively, of the sorbent. The values of K_F and 1/n can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of ln q_e *versus* ln C_e. The three equilibrium curves that were obtained at the three pH values in this study are well represented by the Freundlich isotherm model. When the Langmuir isotherm model was applied to these data, a very good fit was obtained at pH 3 and 7, while some deviation from experimental data was observed at pH 10. But in general, this model is also applicable to describe the experimental equilibrium data for all pH values. The Langmuir constants Q^o and b and Freundlich constants K_F and 1/n at various pH values are displayed in Table-l. It is obvious that the parameters Q° and K_F, which are related to the sorption capacity, increase with a decrease in the pH values. This is consistent with the experimental observation. RI values, which are a measure of goodness-of-fit (Table-1), show that both the Langmuir and Freundlich isotherm models can adequately describe the adsorption data.

TABLE-1
PARAMETERS OF LANGMUIR AND FREUNDLICH ISOTHERM MODELS AT VARIOUS pH VALUES

pH	Langmuir constants			Freundlich constants		
	Q^o (mg/g)	b (1/mg)	R^2	K_F (mg/g)$(1/g)^{1/n}$	1/n	R^2
3	1.824	0.0162	0.972	0.150	0.481	0.980
7	0.925	0.0178	0.963	0.110	0.390	0.910
10	0.633	0.0096	0.941	0.085	0.478	0.948

The kinetic results of Fig. 1 can be used to determine whether adsorption of phenol on to synthesized sorbent obeys kinetically first order or not. The first order Lagergren model for different concentration of phenol is presented in Fig. 5. As it can be seen, plots of log $(q_e - q_t)$ *versus* time are straight lines and confirms applicability of first order kinetic model for adsorption of phenol by synthesized sorbent. In order to determine the rate limiting step for adsorption on to synthesized sorbent, a plot of adsorbate uptake *versus* the square root of time is presented in Fig. 6. Weber and Morris reported that if particle diffusion is the rate-limiting step in the sorption process, this line passes through the origin[29].

As it can be seen, there is a linear relationship between phenol adsorbed and square root of time, so particle diffusion is involved in phenol sorption but the lines do not pass through the origin, this indicates that particle diffusion is not the only rate-limiting mechanism and that some other mechanisms are involved[30].

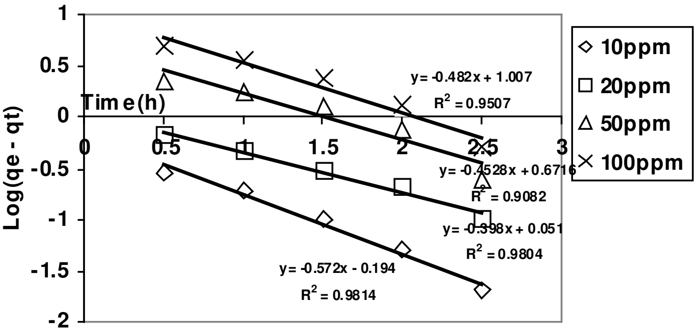

Fig. 5. Lagergren plots for adsorption of phenol in different concentration by synthesized organo-bentonite

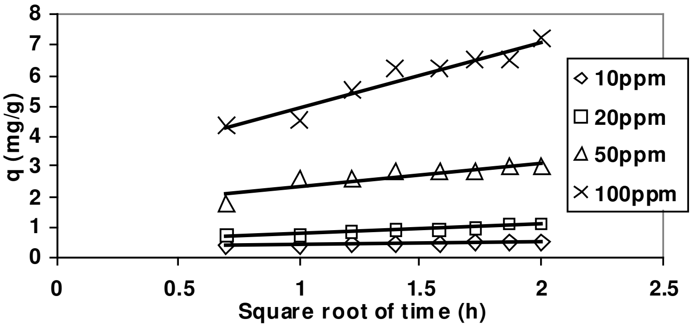

Fig. 6. Amount of phenol adsorbed *versus* square root of time by synthesized low cost organo-bentonite

Conclusion

Natural bentonite without any pretreatment, commercial grade of benzalkonium chloride and tap water were used for synthesis of low cost organo-bentonite. Adsorption behavior of synthesized sorbent was very good for removal of phenol from aqueous solutions. Low cost organo-bentonite could be used as sorbent for organic contaminants in numerous industrial wastewater treatment systems.

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