

Effect of adsorbent concentration to the adsorption of phenol on hexadecyl trimethyl ammonium-bentonite

Saadet Yapar^{a,*}, Vesile Özbudak^a, Ana Dias^b, Ana Lopes^b

^a Ege University, Engineering Faculty, Chemical Engineering Department, 35100 Bornova, Izmir, Turkey

^b Porto University, Engineering Faculty, Chemical Engineering Department, Portugal

Received 5 November 2004; received in revised form 30 January 2005; accepted 31 January 2005

Available online 26 February 2005

Abstract

In this work, it is intended to study the effect of adsorbent concentration on the adsorption of phenol by hexadecyl trimethyl ammonium-bentonite. The experiments were conducted in two groups. The adsorption of hexadecyl trimethyl ammonium bromide (HDTMA) on bentonite was studied in the first group of experiments. It was observed that the all HDTMA was adsorbed by the bentonite, even when the amount used exceeded 100% of cation exchange capacity (CEC). After the modification of bentonite by using HDTMA in an amount equivalent to 100% of CEC, the adsorption experiments were performed at five different adsorbent concentrations ranging from 2 to 10 g/L. A type V isotherm and a non-linear increase in percent removal with adsorbent concentration were observed. The observation of the non-linear relation between the percent removal and adsorbent concentration was attributed to the effect of intra particle interactions and it was represented by a second order polynomial. Several adsorption isotherm equations were applied to the experimental data. Although, the Freundlich equation fitted fairly well, it failed to represent the plateau and the second region that appeared in the isotherm. Therefore, an equation giving the equilibrium concentration as a function of initial and adsorbent concentrations was suggested.

© 2005 Elsevier B.V. All rights reserved.

Keywords: HDTMA; Organo-bentonite; Adsorption isotherm; Adsorbent concentration

1. Introduction

The pollution of water is of serious environmental concern, since many contaminating organic and inorganic materials can be transported by surface and ground waters. Many of these contaminants can be removed by adsorption using various natural and synthetic adsorbents. Due to their excellent adsorption properties, clay minerals are widely used in environmental applications. The removal of phenol is a good example for these applications. There are a number of papers in the literature on the removal of phenol by clays [1–13].

Phenol is actually an ionizable organic compound and it can exist as phenolate and/or a neutral molecular form depending on the pH. Since the negatively charged and hy-

drophilic surfaces of the mineral render it to be less efficient in adsorption, the modified forms of clay are generally used in the removal of phenol. Temperature, time, initial adsorbate concentration, pH, and modification procedures were the parameters investigated. Although it has technical interest, there are only a few papers reporting the effect of the amount of adsorbent [5,10,11]. An increase in the amount of phenol removed with increasing adsorbent concentration was generally observed; Shen [10] and Al-Asheh et al. [11] reported that this increase was limited. That is, a plateau was observed when residual phenol concentration was drawn against sorbent concentration. No correlation between the residual phenol and amount of adsorbent was given in their studies.

In fixed bed columns used for wastewater treatment and environmental remediation, activated carbon is the commonly used adsorbent. However, there are some applications in which organo-clay and activated carbon are used to increase the efficiency of the treatment systems [14]. Therefore, the

* Corresponding author. Tel.: +90 232 388 76 00x125; fax: +90 232 388 76 00.

E-mail address: yapar@eng.ege.edu.tr (S. Yapar).

Nomenclature

a	the parameter of the Freundlich isotherm
C	concentration (mg/L)
k_F	the parameter of the Freundlich isotherm
m	adsorbent concentration (g/L)
Q	adsorbed amount (mg/g)
ΔQ	normalized deviation

Subscripts

eq	equilibrium
i	initial

adsorption characteristics and the effect of the amount of adsorbent on the adsorption are of importance. In our work, the effect of the amount of adsorbent was studied. A correlation between the residual phenol and amount of adsorbent was given in addition to the adsorption isotherm.

2. Experimental

2.1. Materials

Bentonite was obtained from Tokat, Reşadiye region of Turkey. Chemical composition and cation exchange capacity (CEC) of the bentonite were given in a previous study [13]. Coarse-fraction impurities such as iron oxides and silica were removed by subjecting the bentonite dispersions to repeated sedimentation. The layer at the bottom was removed and the upper portions were exposed to sedimentation until no gritty layer remained. After drying at 60 °C, the sample was pulverized to pass through a 595 μm sieve.

Hexadecyl trimethyl ammonium bromide (HDTMA) was purchased from Aldrich Chemical Company Inc. (Milwaukee, USA). It is of 99% purity and used as supplied. Phenol with 99.5% purity was purchased from Merck (Darmstadt, Germany).

2.2. Adsorption of HDTMA

Adsorption experiments were conducted at the initial concentrations corresponding to different treatment amounts. The treatment amount is defined as the ratio of initial concentration to the concentration equivalent to CEC at given conditions. Surfactant solutions were prepared at previously determined concentrations and then 0.1 g of bentonite was added to 100 mL of each solution. The dispersions were shaken in a thermostatic shaker water bath at 20 °C for 24 h. After the shaking period, the dispersions were centrifuged at 5000 rpm. The concentrations of supernatants were determined through the methyl orange method [15]. 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 at the absorption wave length of 401 nm.

2.3. Modification

The organo-bentonite was synthesized by exchanging the interlayer cations of clay suspensions with HDTMA cations. The surfactant in an amount equivalent to 100% of CEC was dissolved in 1 L of distilled water. A total of 20 g of bentonite was added to the surfactant solution at 60 °C. The dispersions were stirred for 3 h at 60 °C. The separated organo-bentonite was washed repeatedly and subjected to Soxhlet extraction with water vapor to remove intercalated alkylammonium bromide. The water vapor extraction was continued until a negligible amount of surface-active agent was observed in the extract phase. The amount of surface-active agent was determined through the methyl orange method. The Soxhlet extraction was followed by freeze-drying.

2.4. Phenol adsorption isotherms

Phenol adsorption isotherms from aqueous solutions were obtained using the batch equilibration technique. Various amounts of adsorbent (0.2, 0.4, 0.5, 0.6, and 1 g) were added to 100 ml of the unbuffered solutions in a concentration range from 50 to 700 mg/L. The pH of the dispersions was measured before and after adsorption. Dispersions shaken for 24 h were placed in polypropylene tubes and then centrifuged. Supernatants collected in dark brown colored bottles were analyzed by in a JASCO 7000 UV spectrophotometer at the absorption wavelength of 269 nm.

In both cases, the adsorption of HDTMA and phenol, linear calibration curves were used and the coefficients of determination exceeded 0.99. The amount adsorbed was determined from the concentration changes. In the case of HDTMA, the results were presented in terms of actual exchanged amount, that is the ratio of adsorbed amount to maximum possible exchanged amount. The maximum possible exchanged amount is the amount of surfactant which is equivalent to the CEC at given conditions.

All the experiments were repeated at least two times.

3. Results and discussion

3.1. Adsorption of HDTMA

The change in the actual exchanged amount of HDTMA with the treatment amount is given in Fig. 1. As shown in the figure, the slope is nearly one and it remains unchanged at the treatments exceeding 100% of the CEC. This result indicates the existence of strong chain interactions beside multilayer formation and also complete surface saturation. When the treatment is equal to 100% of CEC, all of the

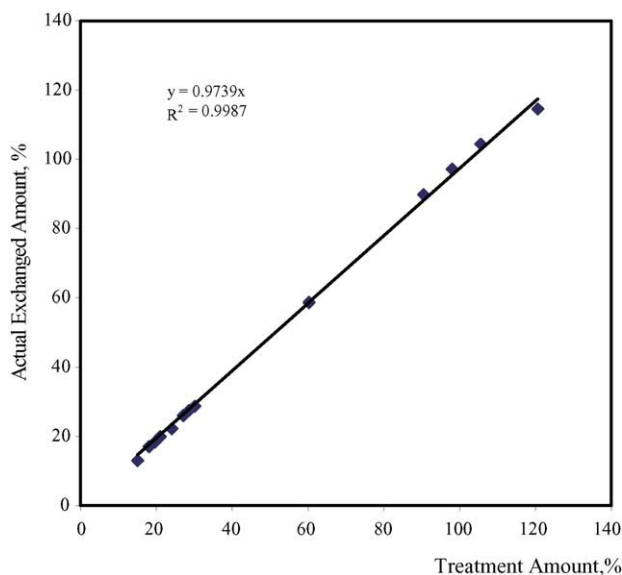


Fig. 1. The change in actual exchanged amount of HDTMA with treatment amount.

neutralizing ions are exchanged with alkylammonium ions and the surface is saturated. For excessive saturations, the chains of cetyl compounds stood erect to the surface [16] and the hydrophobic tails of surfactants forming the second layer are placed between the alkylchains at the first layer. The forces governing the adsorption of the second layer are relatively weak compared to the forces acting on the adsorption of the first layer. Thus, an equilibrium between the solution and solid phase is expected at concentrations exceeding CEC. However, the aqueous phase surfactant concentration is almost zero and it shows that the chain interactions are strong enough to keep HDTMA in the adsorbed layer. This result is in agreement with that obtained by Koh and Dixon [6].

3.2. Modification

Due to its low initial cost, bentonite has an advantage over the synthetic adsorbents. However, it is relatively ineffective in the removal of phenol and it requires modification. Depending on the materials used and the modification procedure, the cost of adsorbent increases. This increase is balanced by an increase in the adsorption efficiency.

The modification procedure used in this study is simple; it involves the removal of coarse-fraction impurities, drying at low temperature, modification with HDTMA and freeze-drying steps. The procedure has almost the same steps as the standard method used in the production of organo-bentonites. Additionally, the mineral is converted into homoionic form but this step was ignored in the present study. This is a factor decreasing the cost of production. In addition to this, the use of less HDTMA can cause a further decrease in the cost since it is rather an expensive chemical. However, the increase in adsorption efficiency is not considerable when the bentonite

is modified with HDTMA at amounts which are less than 100% of the CEC [13]. Therefore, bentonite was modified with HDTMA at 100% CEC.

In addition to the cost of production, the toxicity of HDTMA is another factor to be considered in the practical utilization of organo-bentonite, since the desorption of HDTMA in the solution will create a serious environmental problem. The production procedure involves the Soxhlet extraction and all the intercalated alkylammonium ions are removed at this step. In a previous study, it was reported that HDTMA forms bilayers by adsorbing on the surfaces of the cleavage between the silicate layers when the bentonite is modified by 100% CEC [13]. The procedure used in the preparation was the same in each study. This result indicates even the extreme conditions of extraction (high temperature and prolonged contact time with water) does not cause the desorption of alkylammonium ions adsorbed at the first layer and thus organo-bentonite can be used safely in practical applications.

3.3. Adsorption isotherm

The change in the adsorbed amount of phenol with equilibrium concentrations is given in Fig. 2. Two regions separated by a short plateau are observed in the figure. The increase in adsorbed amount at the second region is rather sharp. This is the characteristic of type V isotherm according to Brunauer classification [17]. Such isotherms are relatively rare and indicative of weak adsorbent–adsorbate interactions [18]. Phenol is adsorbed first by van der Waals attraction to alkyl chains and then the adsorbate–adsorbate forces promote the adsorption of more molecules.

The change in pH before and after adsorption is given in Table 1. Although the pH values increase depending on both the amount of adsorbent used and adsorption, this increase does not cause a significant change in the amount of phenolate. Under these circumstances, phenol is adsorbed in

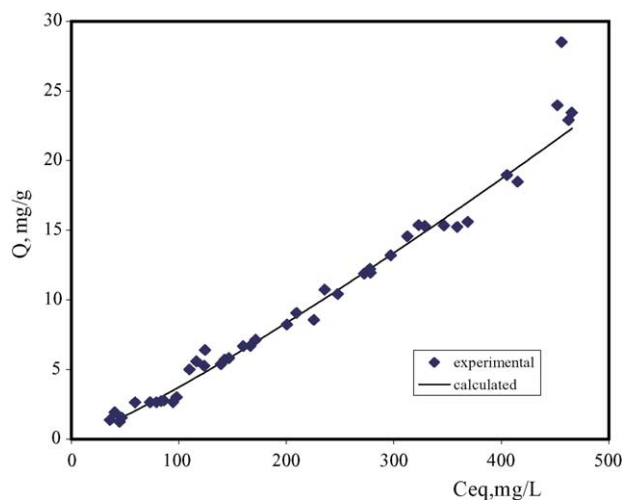


Fig. 2. Adsorption isotherm of phenol.

Table 1
The change in pH values of dispersions

Amount of adsorbent (g)	Initial pH of the dispersion	Final pH of the dispersion
0.2	5.53	6.30
0.4	6.48	6.91
0.5	5.96	6.60
0.6	6.54	7.06

neutral molecular form. However, this increase can be a good indication for adsorption.

3.4. Effect of amount of adsorbent

The removal of phenol is given in Fig. 3 as a function of initial concentration. This figure shows that the removal increases with increasing amounts of adsorbent regardless of initial phenol concentration. The percentage of phenol removed was approximately constant for different amounts of adsorbents over the concentration range studied. Therefore, the average removals were calculated for each adsorbent concentration and the change in percent removal is shown in Fig. 4 as a function of adsorbent concentration. Although the adsorbed amount increases with adsorbent concentration, this increase is not linear. This conforms to the results obtained by Al-Asheh et al. [11] and Al-Malah et al. [5] for CTAB-bentonite. A similar trend was also observed by Shen [10] for the removal of phenol by adsorption flocculation. Although the techniques used in the preparation of adsorbents are different, the observation of the same behavior is because of the effect of the interactions between the particles. Since adsorption occurs on the interlayer surface, it is a diffusion-controlled process involving bulk, intra and interparticle diffusion steps. As reported by Shen [10], adsorption of cationic surfactants causes floc formation. The size of these flocs depends on the amount of particles namely, the increasing adsorbent amounts cause the formation of more and greater sized flocs. As a result, intra particle diffusion resistance increases and this increase is the reason of the gradual decrease observed in the slope of percent removal versus adsorbent concentration curve.

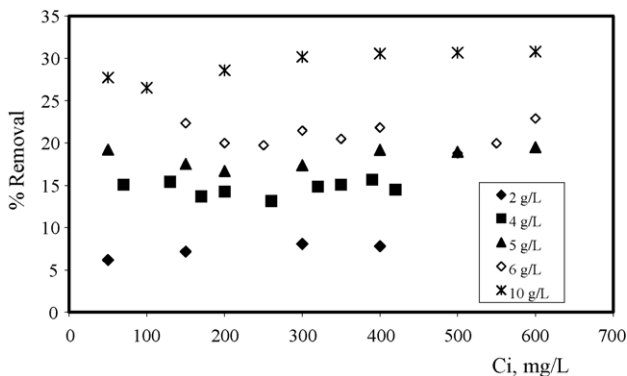


Fig. 3. Change in percent removal with initial concentration.

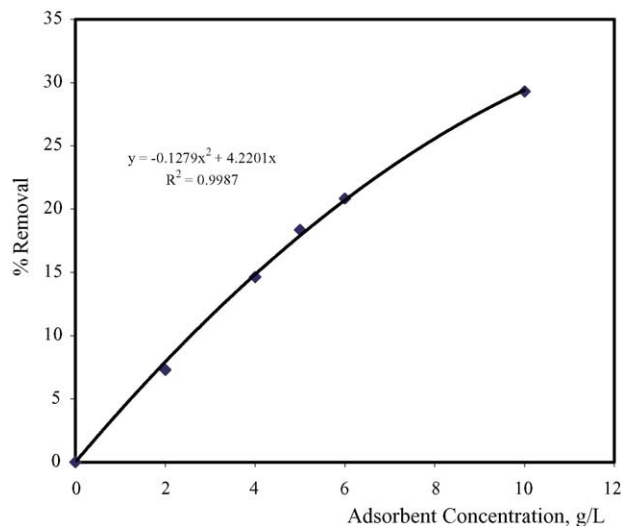


Fig. 4. Change in percent removal with adsorbent concentration.

3.5. Modelling of adsorption behavior

For design purposes, the equilibrium data are represented by either a theoretical or an empirical equation and this equation should contain a small number of parameters. Several isotherm equations including the Freundlich, the Langmuir–Freundlich, the BET, and the Freundlich–BET were applied to the data. The parameters of the equations were found by following the least square fitting routine. The conformity of the equations was checked by calculating the regression coefficient (R^2) and normalized deviation (ΔQ) values. ΔQ was calculated from the following equation [19]:

$$\Delta Q = \frac{1}{N} \sum \left| \frac{Q_{\text{calc}} - Q_{\text{exp}}}{Q_{\text{exp}}} \right| \quad (1)$$

where the subscripts “calc” and “exp” denote the calculated and experimental values, respectively. N is the number of measurements.

As shown in Fig. 2, the Freundlich equation fitted fairly well to the experimental data. Correlation coefficient and ΔQ values were found to be 0.989 and 0.085, respectively. The Freundlich adsorption isotherm is

$$Q = k_F C_{\text{eq}}^a \quad (2)$$

The parameters, k_F and a , were found to be 0.0175 and 1.164, respectively. These values show that the capacity of adsorbent is low and the adsorption bond is weak since k_F represents the capacity and a is related to the strength of adsorption. Beside, the Freundlich constant “ a ” is a measure of the deviation from linearity of adsorption and when $a > 1$, the adsorbed amount changes significantly with small changes in C_{eq} [8]. As mentioned previously type V isotherm has indicative weak adsorbate–adsorbent interactions. These interactions cause the adsorption at low concentration to be small and the results obtained confirm this. However, a close examination of Fig. 2 shows that the Freundlich isotherm

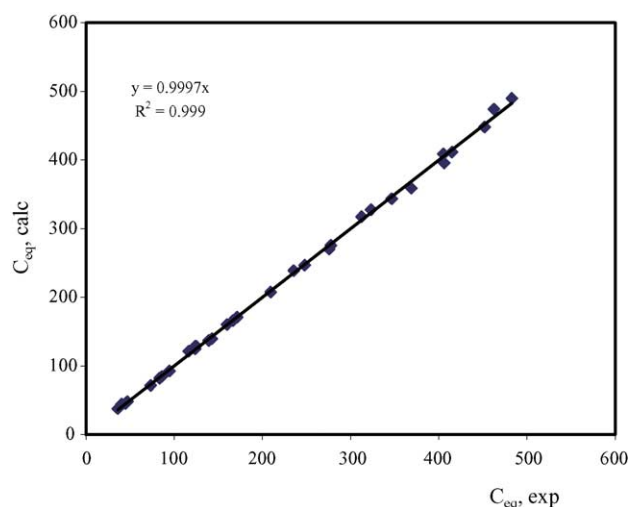


Fig. 5. Comparison of the calculated and experimental C_{eq} values.

fails to represent the plateau region and the relatively sharp increase observed at the second region. In the treatment of wastewater with high phenolic residue, the second region will have a special importance. Therefore, another equation describing the whole concentration range more precisely should be derived. Since the intra particle interactions also have a considerable effect on the adsorption behavior of phenol and thus the amount of adsorbent used should be involved in the model equation suggested. By considering all these factors the following equation was proposed.

$$C_{eq} = 3.764 + 940.65C_i - 26.104(C_i m) \quad \text{for} \\ 0 < C_i \leq 700 \text{ ppm} \quad (3)$$

where C_{eq} is the equilibrium concentration (mg/L) C_i the initial concentration (g/L) and m is adsorbent concentration (g/L).

Regression coefficient and ΔQ values were found to be 0.9989 and 0.0197, respectively. The values calculated from Eq. (2) were drawn against the experimental equilibrium concentrations. As shown in Fig. 5, relationship between $C_{eq,calc}$ and $C_{eq,exp}$ was found to be linear.

4. Conclusions

In this study, it was concluded that the HDTMA is completely adsorbed by the bentonite even when the treatment amount exceeds 100% of the CEC. This result indicates that the chain interactions are strong enough to keep HDTMA in the adsorbed layer.

The adsorption isotherm of phenol points to weak adsorbate–adsorbent interactions causing less adsorption at low concentrations.

A relatively sharp increase observed in the adsorbed amounts at high concentrations is due to the adsorbate–adsorbate interactions promoting the adsorption of more molecules.

There is no linear relation between the removal of phenol and the amount of adsorbent because of the formation of an additional resistance at high adsorbent concentrations. Therefore, the amount of adsorbent needs to be optimized for practical applications.

The Freundlich isotherm failed to represent the whole concentration range. Therefore, an equation describing the equilibrium concentration as a function of initial and adsorbent concentrations was used in the modeling of adsorption behavior.

References

- [1] M.M. Mortland, S. Shaobai, S.A. Boyd, Clay-organic complexes as adsorbents for phenol and chlorophenols, *Clays Clay Miner.* 34 (5) (1986) 581–585.
- [2] M.A.M. Lawrence, R.K. Kukkadapu, S.A. Boyd, Adsorption of phenol and chlorinated phenols from aqueous solution by tetramethylammonium- and tetramethyl-phosphonium-exchanged montmorillonite, *Appl. Clay Sci.* 13 (1998) 13–20.
- [3] T. Viraraghavan, F.M. Alfaro, Adsorption of phenol from wastewater by peat, fly ash and bentonite, *J. Hazard. Mater.* 57 (1998) 59–70.
- [4] F.A. Banat, B. Al-Bashir, S. Al-Asheh, O. Hayajneh, Adsorption of phenol by bentonite, *Environ. Pollut.* 107 (2000) 391–398.
- [5] K. Al-Malah, M.O.J. Azzam, N. Abu-Lail, Olive mills effluent (OME) wastewater post-treatment using activated clay, *Sep. Purif. Technol.* 20 (2000) 225–234.
- [6] S.M. Koh, J.B. Dixon, Preparation and application of organo-minerals as sorbents of phenol, benzene and toluene, *Appl. Clay Sci.* 18 (2001) 111–122.
- [7] P.X. Wu, Z.W. Liao, H.F. Zhang, J.G. Guo, Adsorption of phenol on inorganic–organic pillared montmorillonite in polluted water, *Environ. Int.* 26 (2001) 401–407.
- [8] J.-Q. Jiang, C. Cooper, S. Ouki, Comparison of modified montmorillonite adsorbents part I: preparation, characterization and phenol adsorption, *Chemosphere* 47 (2002) 711–716.
- [9] R.-S. Juang, S.-H. Lin, K.-H. Tsao, Mechanism of sorption of phenols from aqueous solutions onto surfactant modified montmorillonite, *J. Colloid Interface Sci.* 254 (2002) 234–241.
- [10] Y.-H. Shen, Removal of phenol from water by adsorption flocculation using organobentonite, *Water Res.* 36 (2002) 1107–1114.
- [11] S. Al-Asheh, F. Banat, L. Abu-Aitah, Adsorption of phenol using different types of activated bentonites, *Sep. Purif. Technol.* 33 (2003) 1–10.
- [12] Y.-H. Shen, Phenol sorption by organoclays having different charge characteristics, *Colloids Surf. A: Physicochem. Eng. Aspects* 232 (2004) 143–149.
- [13] N. Yilmaz, S. Yapar, Adsorption properties of tetradecyl- and hexadecyl trimethyl-ammonium-bentonites, *Appl. Clay Sci.* 27 (2–3) (2004) 223–228.
- [14] G.B. Beall, The use of organo-clays in water treatment, *Appl. Clay Sci.* 24 (2003) 11–20.
- [15] L.K. Wang, D.F. Langley, Determining cationic surfactant concentration, *Ind. Eng. Chem. Prod. Res. Dev.* 14 (3) (1975) 210–213.
- [16] R.E. Grim, *Clay Mineralogy*, McGraw-Hill, New York, 1968.
- [17] S.J. Gregg, K.S.W. Sing, *Adsorption Surface Area and Porosity*, Academic Press, London, 1982.
- [18] F. Rouquerol, J. Rouquerol, K. Sing, *Adsorption by Powders and Porous Solids, Principles, Methodology and Applications*, Academic Press, London, 1999.
- [19] R.S. Juang, F.-C. Wu, R.-L. Tseng, Adsorption isotherms of phenolic compounds from aqueous solutions onto activated carbon fibers, *J. Chem. Eng. Data* 41 (1996) 487–492.