



Research Article / Araştırma Makalesi

SORPTION ISOTHERMS AND MODELING STUDIES OF HDTMA FOR ADSORPTION ONTO VERMICULITE, PERLITE AND ZEOLITE CLAYS

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Received/Geliş: 15.04.2014 Revised/Düzeltilme: 25.05.2014 Accepted/Kabul: 28.05.2014

ABSTRACT

In this study, as being a cationic surfactant, hexadecyltrimethylammonium bromide (HDTMA-Br) sorption on vermiculite, perlite and zeolite was investigated. Because of using cationic surfactant as softener in the last rinsing, it is discharged as household waste to environmental media at high concentrations. Therefore, removal of cationic surfactants from environmental media is important. Sorption characteristics were searched in terms of sorption capacities and Langmuir, Freundlich, Temkin and Dubinin-Redushkevich isotherm models using batch method. After changing surface of adsorbents to their homoinonic forms by using NaCl, surfaces were become suitable for sorption of positively charged surfactant molecules. HDTMA sorption on vermiculite was best described by Freundlich isotherm model, while Langmuir model was fitted well for perlite and zeolite. Also, experimental and theoretical q_e values were compared and found that they were fitted well with each other. As a result of experiments, it was found that retained HDTMA by adsorbents were 99%, 75% and 96.5% for vermiculite, perlite and zeolite, respectively. It is assumed that the major mechanisms for the sorption of HDTMA on adsorbent are ion exchange between Na ions and HDTMA molecules, electrostatic interaction between negatively charged surface and positively charged surfactant molecules, and also hydrophobic interactions between hydrophobic sides of HDTMA molecules.

Keywords: HDTMA, perlite, sorption, vermiculite, zeolite.

VERMİKÜLİT, PERLİT VE ZEOLİT ÜZERİNE HDTMA ADSORPSİYONUNUN SORPSİYON İZOTERMLERİ VE MODELLEMELERİ

ÖZET

Bu çalışmada, bir katyonik surfaktan olan hegzadesiltrimetilamonyum bromür (HDTMA-Br)'ün vermikülit, perlit ve zeolit yüzeyine adsorpsiyonu incelenmiştir. Katyonik surfaktanların son yıkama suyunda yumuşatıcı olarak kullanılması nedeniyle, evsel atık olarak çevreye yüksek konsantrasyonlarda deşarj edilmektedir. Bu nedenle, katyonik surfaktanların çevresel ortamdan giderimi önem kazanmaktadır. Sorpsiyon karakteristikleri, kesikli sistemde sorpsiyon kapasiteleri ve Langmuir, Freundlich, Temkin ve Dubinin-Redushkevich izoterm modelleri kullanılarak aydınlatılmaya çalışılmıştır. Adsorban yüzeylerinin NaCl kullanılarak homoiyonik forma dönüştürülmesi ile yüzeyler pozitif yüklü surfaktan molekülünü tutmaya elverişli hale gelmiştir. Vermikülit yüzeyine HDTMA sorpsiyonu Freundlich izoterm modeline uygunluk gösterirken, perlit ve zeolit yüzeyine HDTMA sorpsiyonu ise Langmuir izoterm modeline uygunluk göstermiştir. Ayrıca, deneysel ve teorik q_e değerlerinin karşılaştırılması sonucu, bu değerlerin birbirleri ile uyumlu olduğu sonucuna ulaşılmıştır. Denemeler sonucunda, vermikülit, perlit ve zeolit adsorbanlarının HDTMA tutma yüzdeleri sırasıyla %99, %75 ve %96.5 olarak bulunmuştur. Adsorban üzerine HDTMA sorpsiyon mekanizması, yüzeydeki Na iyonları ile HDTMA molekülü arasındaki iyon değişimi, pozitif yüklü HDTMA molekülünün negatif yüklü yüzeye elektrostatik olarak tutunması ve HDTMA moleküllerinin hidrofobik uçları arasındaki etkileşim adımlarından oluştuğu düşünülmektedir.

Anahtar Sözcükler: HDTMA, sorpsiyon, vermikülit, perlit, zeolit.

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1. INTRODUCTION

Adsorption is one of the major processes for the sorption of the cationic surfactants from water. Two mechanisms can be occurred for the adsorption of the cationic surfactants such as, ion-exchange and hydrophobic bonding [1]. Ion-exchange mechanism occurs between the cationic surfactant and positively charged ions on the clay surface. Electrostatic interactions are effective forces for HDTMA sorption on the adsorbent surface. Owing to excess amount of HDTMA in the solution, hydrophobic interactions occur between hydrophobic sides of HDTMA molecules. Parallel to the study of using organo clays to remove dissolved organics from water, it was found that the organo clays developed anion exchange properties when excessive HDTMA was present, which could be used to remove anionic contaminants from water [2]. Besides, organo clays were also used for heavy metal and organic pollutant removal [3-6].

Vermiculite, perlite and zeolite are the adsorbents which are used for the removal of organic and inorganic contaminants from wastewater. Vermiculite has high exchange capacity with 2:1 crystalline structure, in each cell layer structure, the middle layer is an Al-O(OH) octahedral layer, the upper and lower layers being a silicon-oxygen tetrahedron layer [7]. Perlite is a glassy volcanic rock and expands to about 20 times its original volume upon heating within its softening temperature range of 760 to 1090 °C. Perlite is essentially a metastable amorphous aluminum silicate [8]. Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures that contain alumina, silicon, and oxygen. The silicon and alumina atoms are tetrahedral coordinated with each other through shared oxygen atoms. Therefore, natural zeolites have negative charges in their crystal structures, making them suitable surface modification using cationic surfactants [9, 10].

In this study, hexadecyltrimethylammoniumbromide (HDMTA-Br) was used as cationic surfactant. HDTMA sorption is implemented by sorption process using modified natural vermiculite, perlite and zeolite clays. Studies were performed in batch system to investigate the effect of initial solution concentration and equilibrium isotherms. Results were analyzed by Langmuir, Freundlich, Temkin and Dubinin-Redushkevich isotherm models. Theoretical and experimental data were also compared. Sorption of HDTMA on the clays was resulted in producing of the new adsorbents for the anion adsorption.

2. MATERIALS AND METHODS

2.1. Characterization of the Clays

Vermiculite used in the experiments was supplied from Agrekal Agricultural Company, Turkey. Particle size of vermiculite was 1mm. Perlite was supplied from Genper Expanded Perlite Company, Turkey, which had 0.5-1.5 mm particle size. Natural zeolite (clinoptilolite) samples used in the experiments were obtained from Manisa-Gördes, Turkey and the grain size ranging from 0.5 to 1.5 mm.

HDTMA-Br (purity 99%) supplied by Fluka was used for modifying the surface of vermiculite, perlite and zeolite. HNO₃, HCl and NaCl solutions were used as analytical grade reagents.

Concentrated HNO₃ was used for the characterization of the clay minerals. 5 mL of HNO₃ was added onto 5 g of clay mineral and heated until the solution vaporized fully. This procedure was repeated 3 times. At the end of the procedure, the remaining part was taken with distilled water and measured with atomic absorption spectroscopy (Ati Solar Unicam 929 AA Spectrometer) measuring of the cations that the clay mineral includes.

Cation exchange capacity (CEC) of vermiculite was determined by the sodium acetate method [11], where the perlite and zeolite CEC values were determined by ammonium acetate method [12].

2.2. HDTMA Sorption Onto the Clay Minerals

Vermiculite, perlite and zeolite clays were converted to their homoionic forms. Vermiculite, perlite and zeolite clays were mixed with 50 mL of 10% HCl during 30 min and washed with distilled water. Then, hydrogenated clays were shaken with 50 mL of 1M NaCl solution during 30 min. Clay suspensions were filtered and fresh 50 mL of 1M NaCl solution was added on the solid phase. This procedure was repeated two times, followed by washing with distilled water. The solid phase was dried at room temperature.

Homoionic forms of the clay minerals were used for the HDTMA sorption. 0.5 g of Na-vermiculite, 0.05 g of Na-perlit and 1 g of Na-zeolite were mixed with 0.1-100 mmol/L HDTMA solution concentrations. All the samples were shaken during 24 h and washed with distilled water. Total organic carbon (TOC) (Shimadzu TOC-5000A, Kyoto, Japan) analysis has been done to the filtrates.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Clays

Chemical compositions of vermiculite, perlite and zeolite clays are given in Table 1. Cation exchange capacities (CEC) of vermiculite, perlite and zeolite were found as 49 meq/100 g, 5 meq/100 g and 59 meq/100 g, respectively.

Table 1. Chemical composition of vermiculite, perlite and zeolite

Chemical composition (%)			
	Vermiculite	Perlite	Zeolite
SiO ₂	42.67	71.34	67.50
Al ₂ O ₃	17.02	15.01	11.00
MgO	20.79	0.28	0.86
K ₂ O	9.35	4.47	3.31
FeO	6.40	-	-
CaO	0.13	0.50	1.91
Na ₂ O	0.03	3.50	0.50
Fe ₂ O ₃	-	1.53	1.10

Sorption percentage of HDTMA is given in Equation 1:

$$\text{Sorption (\%)} = \frac{c_o - c_e}{c_o} \times 100 \quad (1)$$

where c_o and c_e are defined as initial and equilibrium HDTMA concentration (mmol/L) in the solution. HDTMA sorption percentages on the vermiculite, perlite and zeolite clays are given in Figures 1a, b and c. HDTMA sorption percentage increased with increasing the initial concentration of HDTMA. The maximum HDTMA sorption percentage on the vermiculite, perlite and zeolite was 99%, 75% and 96.5%, respectively. Sorption of HDTMA onto vermiculite clay was occurred between the 2:1 layers, which have negatively charged, while surface and the pores of the perlite and zeolite clays were responsible sites for the sorption of HDTMA. Therefore, the highest sorption percentage was found for vermiculite clay compared with the other clays.

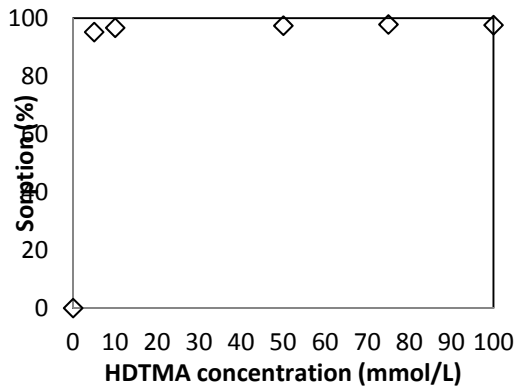


Figure 1a. Sorption of HDTMA on vermiculite

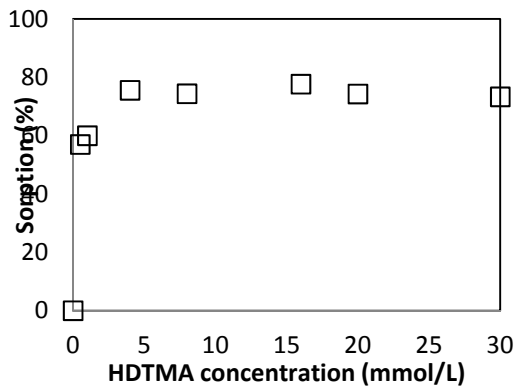


Figure 1b. Sorption of HDTMA on perlite

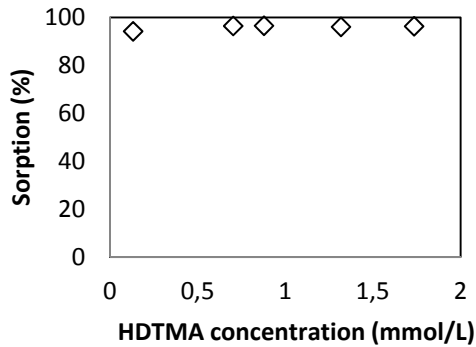


Figure 1c. Sorption of HDTMA on zeolite

Relationship between the amount of HDTMA adsorbed and HDTMA concentration remaining in solution is described by an isotherm. Adsorption isotherms of HDTMA for

vermiculite, perlite and zeolite are shown in Figures 2a, b and c. Sorption capacities of the clays were calculated by using Equation 2:

$$q_e = \frac{c_0 - c_e}{m} \times V \tag{2}$$

where, c_0 and c_e are the initial and equilibrium HDTMA concentration (mmol/L) in the solution, m is the amount of the adsorbent used (g) and V is the volume of the aqueous phase (L).

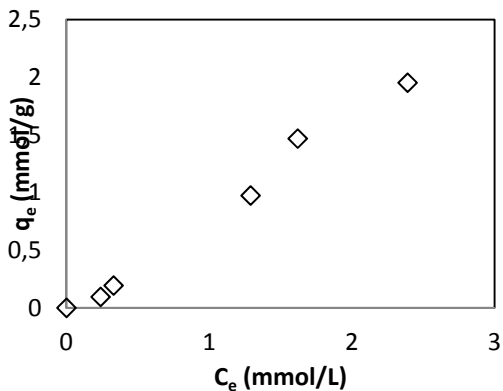


Figure 2a. Sorption isotherm of HDTMA on vermiculite

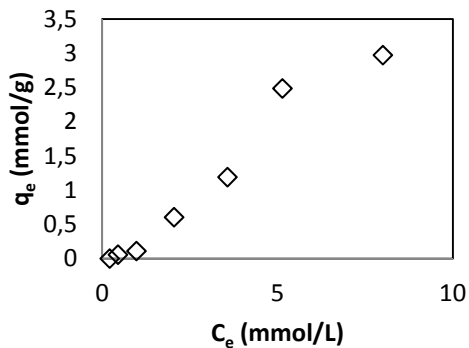


Figure 2b. Sorption isotherm of HDTMA on perlite

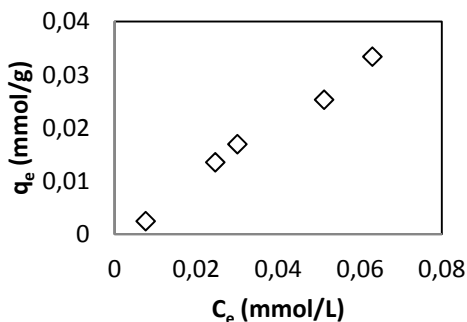


Figure 2c. Sorption isotherm of HDTMA on zeolite

At low HDTMA concentrations, HDTMA molecules were adsorbed on the clay surface by ion-exchange mechanism. In this case, negatively charged clay surface was neutralized by the sorption of positively charged surfactant ions. When the amount of HDTMA molecules was increased, hydrophobic interactions were occurred between hydrophobic sides of HDTMA molecules and second layer was formed on the clay surface. Negative surface charge of the clays reversed to positive by sorption of cationic surfactant molecule.

3.2. Isotherm Models

Sorption isotherms are used to understand the accuracy of the experimental data and make the decision of the data that could be used for the design purposes. Analysing the adsorption capacity of the clays can be done by using Langmuir, Freundlich, Temkin and Dubinin-Redushkevich isotherm models.

Langmuir isotherm model describes monolayer sorption of the adsorbate on the adsorbent surface. Langmuir isotherm equation is given in Equation 3 [13]:

$$q_e = \frac{Q_m b c_e}{1 + b c_e} \tag{3}$$

where, q_e is the amount of HDTMA adsorbed at equilibrium (mmol/g), c_e is the equilibrium HDTMA concentration (mmol/L), Q_m (mmol/g) is the amount of HDTMA per gram of adsorbent which is needed to occur a monolayer on the adsorbent, b is a constant related to adsorption energy and R^2 is the correlation coefficient.

This equation can be rearranged to the following linear form shown in Equation 4 and calculated parameters are given in Table 2.

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{b Q_m} \times \frac{1}{c_e} \tag{4}$$

Freundlich isotherm model is applicable for multilayer sorption of the components in the solution. This empirical isotherm can be used for a non-ideal sorption which indicates the heterogeneity of the surface. The Freundlich adsorption isotherm can be written as shown in Equation 5 [9, 10].

$$q_e = K_F \times c_e^{1/n} \tag{5}$$

where K_F is a constant related to adsorption capacity, $1/n$ is a constant related to adsorption intensity and R^2 is the correlation coefficient.

This equation can be rearranged to the following linear form as given in Equation 6 and calculated parameters are given in Table 2.

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \tag{6}$$

Temkin and Pyzhev studied the heat of adsorption and the adsorbent-adsorbate interactions on surface. Temkin isotherm equation is given in Equation 7 and calculated parameters are given in Table 2 [14].

$$q_e = \frac{RT}{b} \ln K_t + \frac{RT}{b} \ln c_e \tag{7}$$

where, T (K) is the absolute temperature, R is the universal gas constant (8.314 kJ/mol.K), K_t is the equilibrium binding constant (L/mmol), b is the variation of adsorption energy (kJ/mol) and R^2 is the correlation coefficient.

Dubinin-Redushkevich isotherm model is related to porous structure of the sorbent. Equations 8 and 9 show the Dubinin-Redushkevich equations [14]. Table 2 shows the isotherm model constants.

$$\ln q_e = \ln Q_m - B\varepsilon^2 \tag{8}$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{c_e} \right) \tag{9}$$

B is the mean free energy of the sorbate that transfers from infinite distance in the solution to the solid surface and R^2 is the correlation coefficient [14].

Table 2. Isotherm model constants

Clay	Langmuir	Freundlich	Temkin	Dubinin-Redushkevich
Vermiculite	$Q_m = 0.402$ $b = 2.27$ $R^2 = 0.95$	$K_F = 0.858$ $n = 0.771$ $R^2 = 0.99$	$b = 3.242$ $K_t = 4.104$ $R^2 = 0.94$	$B = 0.181$ $Q_m = 1.812$ $R^2 = 0.98$
Perlite	$Q_m = 0.254$ $b = 2.55$ $R^2 = 0.98$	$K_F = 0.683$ $n = 0.795$ $R^2 = 0.97$	$b = 2.624$ $K_t = 2.998$ $R^2 = 0.88$	$B = 0.227$ $Q_m = 2.115$ $R^2 = 0.84$
Zeolite	$Q_m = 0.219$ $b = 2.71$ $R^2 = 0.99$	$K_F = 0.960$ $n = 0.823$ $R^2 = 0.98$	$b = 0.002$ $K_t = 0.990$ $R^2 = 0.93$	$B = 9 \times 10^{-5}$ $Q_m = 0.035$ $R^2 = 0.94$

Determination coefficient, R^2 , was applied to determine the relationship between the experimental data and the isotherm model in most studies [15]. According to R^2 values Freundlich isotherm model was fitted well for HDTMA sorption onto the vermiculite clay. Langmuir model represents a better fit to the experimental data for the sorption of HDTMA onto the perlite and zeolite surfaces. Alkan et al. studied CTAB sorption on perlite and experimental data was modeled by using Langmuir and Freundlich isotherm models. They found that Freundlich isotherm model was best described the experimental data [8]. Lin et al. studied sorption of different cationic surfactants (CPC, CTAC, HDTMA, DTAB, MTAB) on activated

carbon and they applied Langmuir isotherm model. Determination coefficients of Langmuir isotherm models were found between 0.92-1 [16].

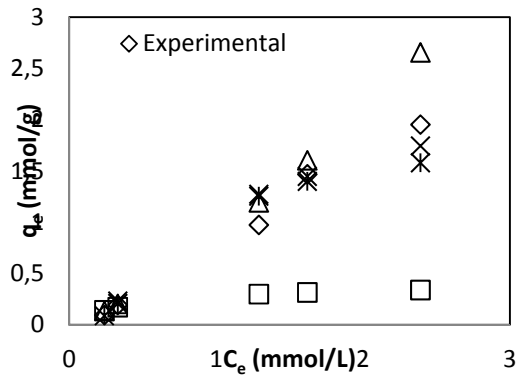


Figure 3a. Sorption isotherms of HDTMA on vermiculite clay

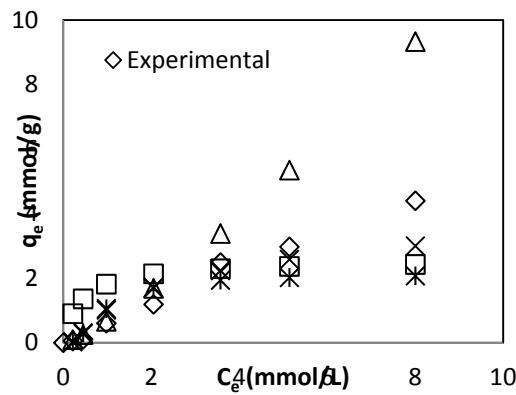


Figure 3b. Sorption isotherms of HDTMA on perlite clay

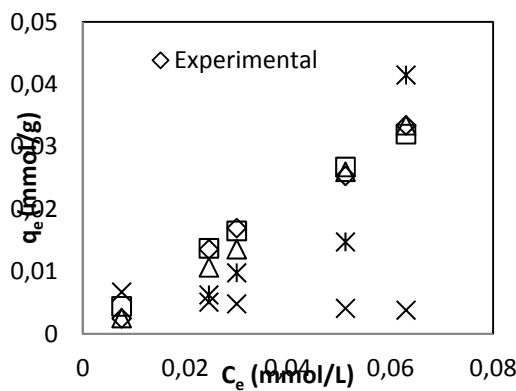


Figure 3c. Sorption isotherms of HDTMA on zeolite clay

Experimental and theoretical q_e values according to the isotherm models are shown in Figures 3a, b and c. For the vermiculite and perlite clays, Temkin and Dubinin-Redushkevich isotherm models were well fitted with the experimental q_e values. Langmuir isotherm model gave the lower q_e values than the experimental ones for the vermiculite, while the Freundlich isotherm model data fitted well with the experimental ones. Langmuir isotherm model gave the higher q_e values for the perlite and zeolite clay.

4. CONCLUSION

Vermiculite, perlite and zeolite's negatively surface charges were converted to positive at high HDTMA loading levels. HDTMA molecules adsorbed on the surface by electrostatic interactions and formed bilayer by interaction of hydrophobic sides. Sorption of HDTMA onto vermiculite was best described by Freundlich isotherm model, while HDTMA sorption on perlite and zeolite surfaces was fitted well with Langmuir isotherm model. Surface coverage of HDTMA onto vermiculite surface was 99%, while it was 75% for perlite. 96.5% of HDTMA sorption was obtained for the zeolite surface.

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