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Equilibrium and kinetics studies of 2,4,5-trichlorophenol adsorption onto organophilic-bentonite

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ABSTRACT

The adsorption of 2,4,5-trichlorophenol (2,4,5-TCP) from aqueous solutions onto the crude bentonite modified with hexadecyltrimethylammonium-bromide (HDTMAB) have been studied. The parameters that affect the 2,4,5-TCP adsorption onto modified bentonite (BHDTMA), such as contact time, solution pH, and temperature have been investigated and optimized conditions determined. Three kinetic models have been evaluated in order to attempt to fit the experimental data, namely the pseudo-first order, the pseudo-second-order and the intraparticle model. The results show that the pseudo-second-order kinetic model generates the best agreement with the experimental data for the adsorption system. Adsorption equilibrium data of 2,4,5-TCP on BHDTMA were analyzed by Langmuir, Freundlich and Langmuir-Freundlich isotherm models. The results indicate that the Langmuir-Freundlich model provides the best correlation of experimental data. The maximum capacity of BHDTMA at 293 K was founded around 72 mg/g. The thermodynamic parameters such as a free energy, enthalpy and entropy of adsorption was calculated. The negative values of ΔG° and ΔH° indicate the spontaneous and exothermic nature of the process.

Keywords: Adsorption; Bentonite; Organophilic-bentonite; 2,4,5-Trichlorophenol; Kinetics; Thermodynamic

1. Introduction

Chlorophenolic compounds such as 2,4,5-trichlorophenol (2,4,5-TCP); 2,4,6-trichlorophenol; 2,4-dichlorophenol and other phenolic compounds derivatives belong to a group of common environmental contaminants. Chlorophenols are mainly produced in chemical industries, such as petroleum refineries, plastics, pharmaceuticals and pesticides. Even low concentrations can be an obstacle to the use or reuse of water. Phenols give an unpleasant taste and odor to drinking water and can exert negative effects on different biological processes. Phenol concentrations of over 2 mg/L are toxic to fish and concentrations between 10 and 100 mg/l result in death of aquatic life within 96 h [1]. Most of these compounds are known or suspected to be human carcinogens. Toxicity generally increases with the degree of chlorination and it has been reported that the OH group plays an important role in the toxicity of chlorophenols to fish. Various physicochemical methods have been proposed for the treatment of wastewaters containing phenolic wastes [2–7]. It is now widely recognized that sorption processes provide a feasible method for the removal of pollutants from wastewaters. Great effort has been exerted to develop new sorbents and

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stabilizers (e.g., organoclays, activated carbon and surfactant-modified zeolites) to immobilize nonionic organic contaminants in situ [8–12]. Adsorption onto activated carbons in the form of grains or powder is a well-known process for organic contaminant removal [13]. Due to their porous nature and high internal specific surface areas activated carbons have favourable properties for adsorption. However, the high cost and recovering activated carbon particles from treated water may be difficult for adsorption. There has been a continuous attempt for locally available and cheaper adsorbents for removal of a variety of organic compounds. Some studies [14–18] illustrate the important need of low cost clay materials treated by some chemical or physical processes as adsorbents for removal of organic pollutants and pesticides from water and wastewater. Recently, organoclays, such as octadecyl-trimethylammonium clays, hexadecyltrimethylammonium (HDTMA) clays, tetramethylammonium clays have been used to remove various NOCs, such as benzene, toluene, alkylbenzene and chlorinated phenols from water [14–21]. Phenols and chlorophenols, which are representatives of a very important pollutant class, were of interest. Backhaus et al. [22] studied the adsorption behavior of 2,4-dichlorophenol on Ca-montmorillonite and its pH dependence. The study concluded that the increasing pH reduces 2,4-dichlorophenol adsorption due to Coulomb repulsion and solubility effects. Mortland et al. [16] studied the adsorption of phenol, 3-chlorophenol, 3,5-dichlorophenol, 3,4,5-trichlorophenol and 2,4,6-trichlorophenol. The obtained results show generally a good adsorption of all used chlorinated phenols when montmorillonite is exchanged by HDTMA. Bingjun Pan et al. [23] examined the removal of phenol from aqueous solution using a porous acrylic ester polymer (Amberlite XAD-7) and shows that adsorption was favourable at acidic solution pH.

The aim of this work is to study the adsorption of 2,4,5-TCP compound from aqueous solutions onto exchanged Algerian bentonite. Surfactant-modified clay can be synthesized by exchanging adsorbed Na^+, Ca^+, Mg^+, etc. on the clay surface with a surfactant (HDTMA). As the bentonite is progressively intercalated by a surfactant, the surface properties of the clay change considerably, and so does the ability of organo-bentonite to remove organic contaminants from water. Previous research showed that organo-bentonite [24–26] is one of the most powerful sorbents used to remove chlorophenol from waste waters.

In this research we want to evaluate the capabilities of surfactant-modified clay for selective removal of 2,4,5-TCP compound from water in the presence of a long-alkyl-chain organic cation (HDTMA). Sorption of this pollutant onto the surfactant-modified clay is characterized to examine in detail his sorptive characteristics and mechanisms.

2. Materials and experimental methods

2.1. Adsorbents

The clay used in this study was Algerian bentonite from Roussel in Maghnia (West Algeria). For this clay material, the cation exchange capacity CEC = 90 meq/100 g was assumed [27]. It has a specific surface area of 80 m^2/g. Hexadecyltrimethylammonium bromide (HDTMAB) was analytical grade greater than 99% purity and purchased from Aldrich Chemical.

2.2. Preparation of surfactant-modified bentonite

The clay was firstly treated with 1 M HCl solution one time and washed several times with distilled water. The H-bentonite was then modified by HDTMAB with the molecular formula $C_{19}H_{42}N^+$. Surfactant-modified bentonite was prepared by adding amounts of surfactant equivalent to 100% of the value of CEC. The main objective consists to enhance capacities adsorption of this adsorbent material. In this operation, this cationic surfactant can be adsorbed onto negatively charged clay surfaces and is not influenced by solution pH, since it is a quaternary ammonium compound. The surfactant HDTMA consists of a 16-carbon chain tail group attached to a trimethyl quaternary amine head group with a positive permanent (+1) charge. It is water-soluble and exists as individually dissolved molecules in solutions with a concentration below the critical micelle concentration (CMC) or as micelles above the CMC of 9×10^{-4} M at 25°C. The surfactant was dissolved in 1 L of distilled water at approximately 80°C and stirred for 3 h. A total of 10 g of H-bentonite was mixed to the surfactant solution. The dispersion was stirred for 3 h at 80°C. The separated organo-bentonite was washed until the supernatant solution was free of bromide ions, as indicated by the AgNO3 test. The obtained modified clay noted BHDTMA was oven-dried at 110°C until the water was completely evaporated. This organoclay was then stored in airtight containers before used in sorption experiments.

2.3. Adsorbate

The adsorbate using in this study is the 2,4,5-TCP. This chemical used without any purification is analytical grade greater than 99% purity and purchased from Aldrich Chemical.

2.4. Kinetic studies

In this part of the kinetic study, some parameters such as effect of initial pH (2, 4, 6, 8, 10), temperature (20, 30, 40, 50°C) were investigated. The pH was adjusted by adding a few drops of dilute NaOH or HCl before each experiment and it measured after. It observed that no significant change in pH value during adsorption. BHDTMA samples were dispersed in 50 ml of 2,4,5-TCP with an initial concentration of 100 mg/L and stirred with agitation speed of 100 rpm. After each time of contact a sample was removed and centrifuged. The 2,4,5-TCP concentrations were determined with a Shimadzu UV-1700 UV-visible spectrophotometer at 290 nm for dispersions at pH(2; 4; 6) when the fraction of phenolate was very low. The determination was done at 310 nm for dispersions at pH(8; 10) when the fraction of phenolate was dominant. The amount of TCP adsorbed was derived from the initial and final concentrations in the liquid phases. All experiments were run in triplicate to ensure reproducibility. TCP uptake by BHDTMA was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t).V}{m}, \tag{1}$$

where q_t is the amount of adsorbed TCP at time t (mg/g); V is the volume of solution (L),

C_0 and C_t initial and at time t TCP concentration, respectively, (mg/L) and m is the mass of adsorbent (g).

2.5. Adsorption isotherms

A constant volume of 2,4,5-TCP solution (50 ml) with varying initial concentrations of TCP (10–180 mg/L) were mixed with a constant amount of BHDTMA (50 mg). The dispersions were maintained at constant pH = 2.0 over 300 min. The 2,4,5-TCP q_e loading (in mg per unit mass of BHDTMA) was obtained by the following equation:

$$q_e = \frac{(C_0 - C_e).V}{m}, \tag{2}$$

where C_0 (mg/L) and C_e (mg/L) are initial and equilibrium 2,4,5-TCP concentration, respectively; V (L) is the volume of solution, and m (g) is the mass of adsorbent.

3. Results and discussions

3.1. Kinetic modelling

Kinetic studies of the removal of 2,4,5-TCP onto BHDTMA were concerned with obtaining essential information to enable the adsorbent to be used in practical treatment systems. Generally, three steps are involved during the process of sorption by porous-adsorbent particles [28]: (i) external mass transfer, (ii) intraparticle transport within the particle (iii) chemisorption. In order to investigate the mechanism of adsorption of 2,4,5-TCP onto BHDTMA the constants of sorption and intraparticle diffusion were determined in terms of the pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

3.1.1. Pseudo-first-order

The rate constant of adsorption is determined from the pseudo-first-order rate expression given by Lagergren [29]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \tag{3}$$

where k_1 (mn^{-1}) is the first-order rate constant of adsorption, q_e (mg/g) is the amount of adsorbed at equilibrium, and q_t is the amount adsorbed at time t. After integration, with the initial conditions $q_t = 0$ at $t = 0$, the equation becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

The values of q_e and k_1 where calculated from slope and intercept of plot ln(q_e−q_t) against time t (figure no showed). If the plots were found to be linear with good correlation coefficient, it indicated that Lagergren's equation is appropriate to 2,4,5-TCP adsorption on BHDTMA. So, the adsorption process is a pseudo-first-order process.

3.1.2. Pseudo-second-order

Another simple kinetic model which is the pseudo-second-order kinetics model [30,31] is expressed by the equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \tag{5}$$

where k_2 (g/mg/min) is the pseudo-second-order rate constant of adsorption of 2,4,5-TCP on BHDTMA. The following integrated form can be obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t. \tag{6}$$

By plotting t/q_tvs. t, (Fig. 1B) q_e and k_2 can be determined from slope and intercept.

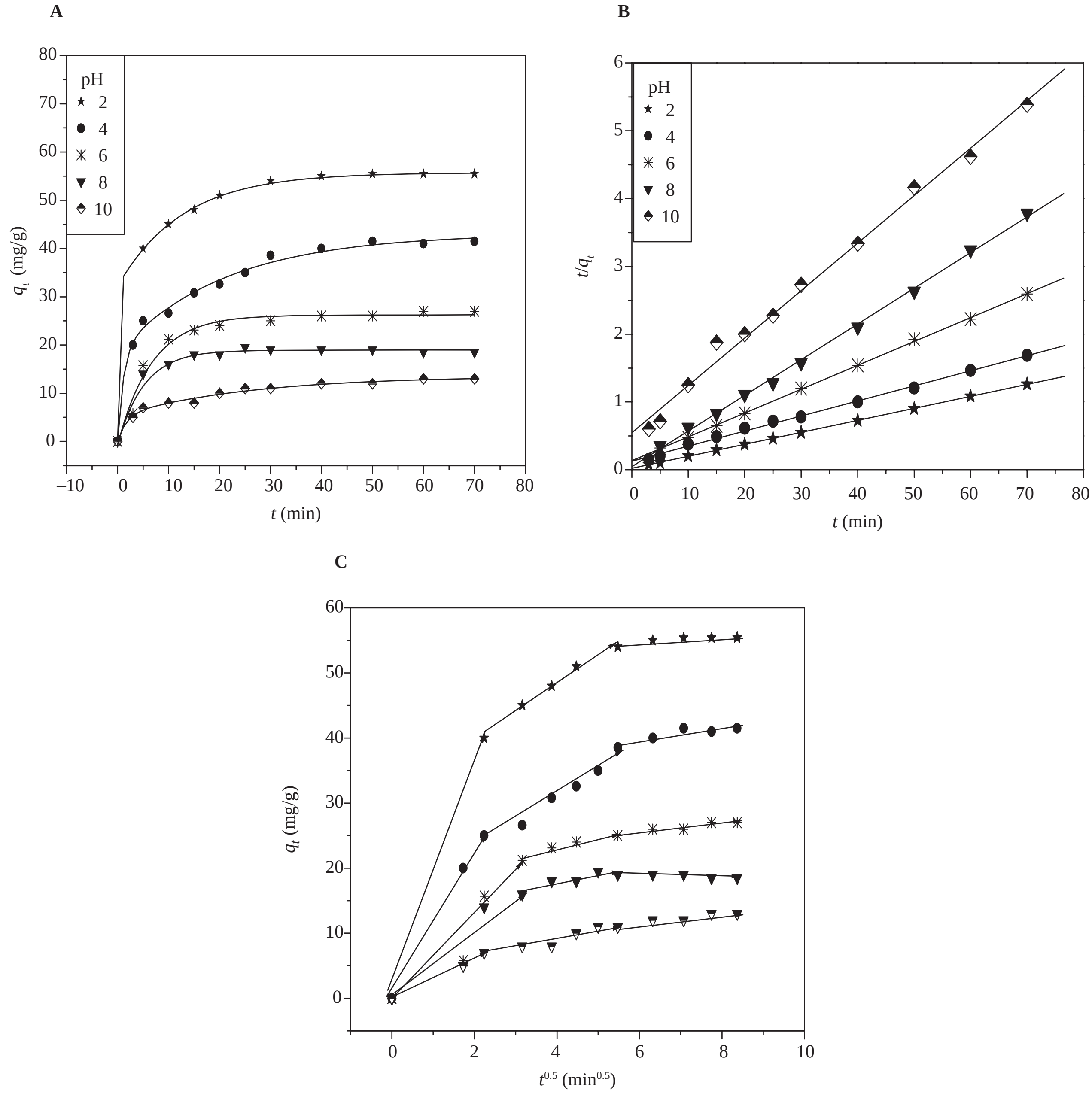

Fig. 1. (A) Kinetic adsorption of 2,4,5-TCP onto BHDTMA; (B) Pseudo-second-order kinetic model; (C) Intraparticle diffusion plot ($m = 50$ mg; $V = 50$ mL; Ag. Speed =100 rpm; $C_0 = 100$ mg/L; $T = 20$ °C).

3.1.3. Intraparticle diffusion model

The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled either by one or more steps, film or external diffusion, pore diffusion, surface diffusion, or a combination of more than one step. The rate parameter of intraparticle diffusion can be defined as:

$$q_t = k_i t^{0.5} \div C \tag{7}$$

where q_t is the amount of 2,4,5-TCP adsorbed at time t, C the intercept and k_i (mg/g min$^{0.5}$) is the intraparticle rate constant. Fig. 1C shows that plots q_t against $t^{0.5}$ consist of two or three separate linear regions, which confirms that the intraparticle diffusion is not the only process involved in this system, since a simple linear plot would be observed if these where the case. It has been suggested that the first one can be attributed to external diffusion, the second to intraparticle diffusion and the third to chemical reaction.

The first straight line signifies that the TCP molecules are transported to the external surface of the organo-bentonite particle through film diffusion and its rate is very fast. The second straight line indicated that intraparticle diffusion through pores is involved in the process. Both the line does not pass through the origin; it concludes that both film diffusion and intraparticle diffusion are simultaneously occurring during the adsorption of TCP onto BHDTMA.

3.2. Effect of contact time and pH

The adsorption of 2,4,5-TCP on BHDTMA is studied as a function of a contact time in order to find out the equilibrium time for maximum adsorption. The results (Fig. 1A) show that equilibrium time required for the process was 40 min for dispersions at pH(2, 4, 6) and 20 min for pH(8, 10) indicating a very fast adsorption process. At the beginning the 2,4,5-TCP is adsorbed by the exterior surface of adsorbent and reached saturation, after the 2,4,5-TCP ions entered into the pores of adsorbent by the interior surface of the particles. This phenomenon takes relatively long contact time.

As the pH is an important variable affecting the solute adsorption, the removal of 2,4,5-TCP onto BHDTMA was examined at different pH ranging from 2.0 to 10.0 with initial concentration of 100 mg/L and at temperature of 20°C.

It can be seen from Fig. 1A that the amount of adsorbed 2,4,5-TCP on BHDTMA decreases with increasing pH according to others results founded by some authors [32,33]. The highest adsorption of 2,4,5-TCP on BHDTMA is occurred at pH(2; 4) but at pH (6; 8; 10) the adsorbed amount decreased by approximately half. This effect can be explained by considering the theoretical distribution of various phenol species in aqueous solution. Most phenols (POH) are considering like weak acids in aqueous solution [34,35]. The dissociation of hydrogen ion from the phenol molecules strongly depends on the pH level of solution. The molecules species (POH) is the predominant in acidic solutions, whereas the ionic species (PO^-) predominates in alkaline solutions. At acidic solutions, more protons are available, thereby increasing electrostatic attractions between molecular 2,4,5-TCP and the positively charged adsorption sites causing an increase in the adsorption of 2,4,5-TCP. As the pH increase, a negative charges on the organo-bentonite surface increase and blocking of pores by (probably hydrated) basic sites-protons, in this case the adsorption of 2,4,5-TCP is not favourable because it is also negatively charged (PO^-) and there may be also competition between the $OH^\bullet$ ions and 2,4,5-TCP.

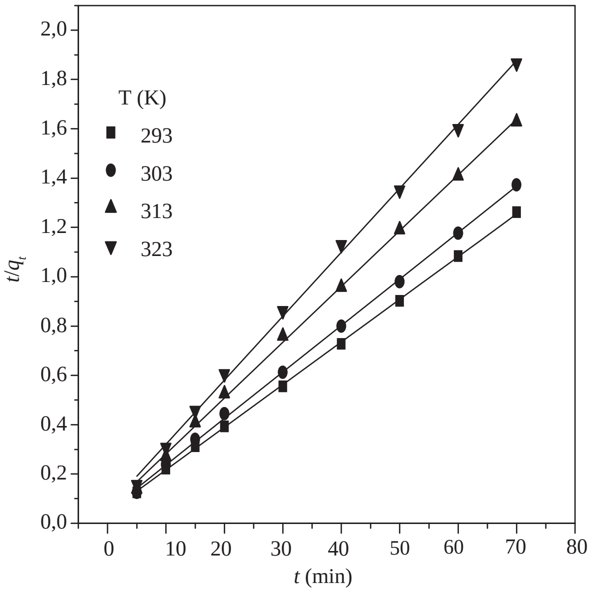

Fig. 2. Pseudo-second-order kinetic model: adsorption of 2,4,5-TCP onto BHDTMA.

3.3. Effect of temperature

The effect of temperature on adsorption capacity of BHDTMA was studied because the temperature is a highly significant parameter in the adsorption. The maximum of adsorption is obtained at 20°C. The decrease of adsorption capacity with increasing in temperature indicated that the adsorption of 2,4,5-TCP onto BHDTMA is exothermic in nature. A similar trend was also observed by Jian-Ping Wang et al. [28]. The decrease in adsorption with the rise of temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate species and also between the adjacent molecules of the adsorbed phase. In other hand, solubility of chlorophenols increases with temperature so adsorption decreases.

3.4. Mechanism

Table 1 presents the results of fitting experiment data. It can be seen that the correlation coefficient is $0.993 < R^2 < 0.999$ for the pseudo-second-order model, $0.771 < R^2 < 0.980$ for the pseudo-first-order model and $0.815 < R^2 < 0.987$ for the intraparticle model, which indicates that the pseudo-second-order equation is better in describing the adsorption kinetics of 2,4,5-TCP by BHDTMA. The experimental ($q_{e,exp}$)

Table 1
Kinetic models parameters obtained in adsorption of 2,4,5-TCP onto BHDTMA

		Pseudo-first-order				Pseudo-second-order			Intra-particle diffusion		
T (K)	pH	$q_{e,exp}$	$q_{e,cal}$	k_1	R^2	$q_{e,cal}$	k_2	R^2	k_i	C	R^2
293	2	55.4	38.8	0.114	0.980	7.7	70.42	0.999	4.35	30.88	0.987
303	2	51.0	27.7	0.086	0.906	53.1	72.78	0.999	2.71	33.57	0.972
313	2	43.0	17.6	0.062	0.884	44.2	92.32	0.999	1.05	33.36	0.885
323	2	37.5	14.7	0.062	0.771	38.6	108.64	0.998	0.80	29.95	0.815
293	2	55.4	38.8	0.114	0.980	57.7	70.42	0.999	4.35	30.88	0.987
293	4	41.5	30.5	0.071	0.977	45.0	39.32	0.996	4.17	14.59	0.966
293	6	27.0	16.3	0.066	0.896	29.7	54.97	0.999	3.72	8.23	0.924
293	8	18.5	17.2	0.198	0.938	19.8	178.87	0.998	1.92	9.90	0.962
293	10	13.0	9.2	0.051	0.941	14.3	90.09	0.993	1.42	3.49	0.881

q_e (mg g^{-1}), k_1 (min^{-1}), k_2 (10^{-4} (g mg^{-1} min^{-1}), k_i (mg g^{-1} min$^{-1/2}$), C (mg g^{-1}).

values agree well with the calculated ones obtained from the pseudo-second-order kinetic models, and a good fitting of experimental data to pseudo-second-order equation suggests that the overall rate of adsorption process appears to be controlled by chemisorption mechanism. In addition, the pseudo-second-order model predicts the behaviour over whole range of the adsorption process.

3.5. Equilibrium isotherms

Equilibrium studies were carried out in order to determine the optimum conditions for maximum 2,4,5-TCP removal by BHDTMA. This represents the quantity of 2,4,5-TCP adsorbed q_e (mg/g) against the equilibrium concentration in the solution. It corresponds to the equilibrium distribution of 2,4,5-TCP between the aqueous and solid phases at different concentrations. Fig. 3 shows the equilibrium isotherm at temperature 20°C and initial concentrations (10–180 mg/L) which indicates that the amount of adsorbed 2,4,5-TCP increases with increasing the equilibrium concentration. Equilibrium models were used in an attempt to fit the experimental data: the Langmuir model (Eq. (8)), the Freundlich model (Eq. (9)) and the Langmuir-Freundlich model (Eq. (10))

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}, \tag{8}$$

$$q_e = K_F C_e^n, \tag{9}$$

$$q_e = \frac{q_{mLF} K_{LF} C_e^n}{1 + K_{LF} C_e^n}, \tag{10}$$

where q_m; K_L and q_{mLF}; K_{LF} are constants related to the loading capacity and the free energy of a Langmuir and Langmuir-Freundlich equations, respectively; K_F and n are the Freundlich temperature-dependent constants; C_e is the equilibrium concentration (mg/L) and q_e (mg/g) is the amount adsorbed 2,4,5-TCP at equilibrium.

Fig. 3 shows that the Langmuir-Freundlich model gives a better fit to the experimental isotherm than either the Langmuir or Freundlich isotherms on the basis of regression coefficients ($R^2_{L-F} = 0.972$; $R^2_L = 0.904$; $R^2_F = 0.857$) and the best fit Langmuir-Freundlich parameters are $q_{mLF} = 72.14 \pm 3{,}96$ mg/g; $K_{LF} = 0.032 \pm 0.0029$ L/mg and $n = 2.574 \pm 0.36$.

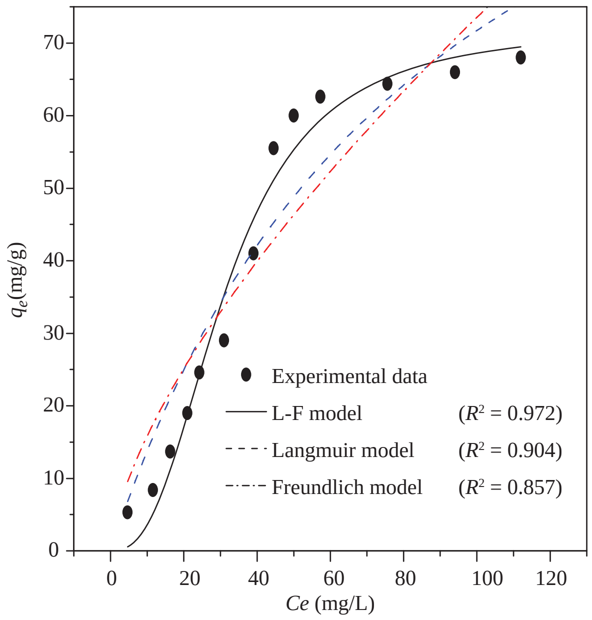

Fig. 3. Equilibrium isotherms for adsorption of 2,4,5-TCP onto BHDTMA (pH = 2; V = 50 mL; T = 20°C; $w_{adsorbent} = 50$ mg; Ag. Speed = 100 rpm).

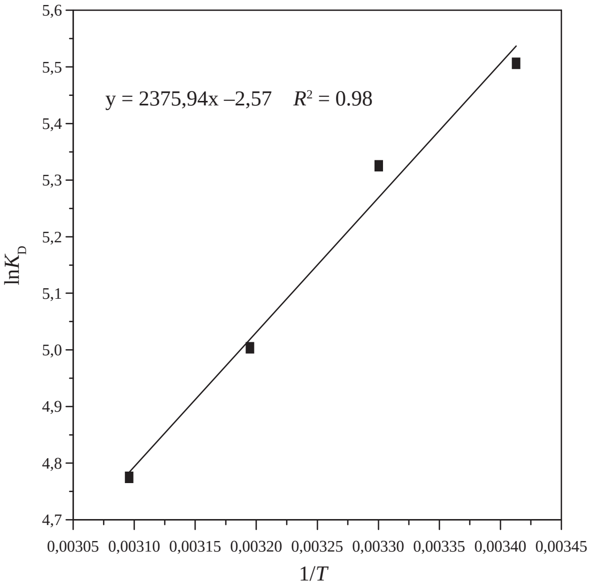

Fig. 4. Van 't Hoff plot for absorption of 2,4,5-TCP onto BHDTMA.

The high levels of adsorption indicate that the 2,4,5-TCP attracted sufficiently to the hydrophobic surfaces of BHDTMA, it must have penetrated into interlayer surfaces. In water solvent, as the number of chlorines on the phenol structure was increased, phenolics compounds was not interacted with water (hydrogen bonding) and the greater was the adsorption on the hydrophobic matrix. Here, adsorbate–adsorbent interaction was relatively strong, probably due to hydrophobic interaction and positively charged of adsorbent surface at pH 2.

The variation in the extent of adsorption with respect to temperature has been explained on the basis of thermodynamic parameters, changes in standard free energy ΔG^0, enthalpy ΔH^0 and entropy ΔS^0. These were calculated by using the following equation:

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}, \tag{11}$$

where K_D is the distribution coefficient of the adsorbent and equal to q_e/C_e, ΔH^0 is the standard enthalpy, ΔS^0 is the standard entropy, R is the gas constant and T is the temperature. The plot of ln K_D versus $1/T$ (Fig. 4) is linear with slope and intercept giving values of ΔH^0 and ΔS^0. These values were used to compute ΔG^0 from the Gibbs free energy change relation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \tag{12}$$

The negative ΔG^0 values (−13.5 kJ/mole) indicate that the adsorption process was feasible and spontaneous. The change of Gibbs free energy for the physical adsorption is generally in the range of −20 to −50 kJ/mol, and that for the chemical adsorption is in the range of −80 to −400 kJ/mol [31]. The values of ΔG^0 at 293 K in this study indicated that the adsorption of 2,4,5-TCP onto BHDTMA could be considered as a physical adsorption enhanced by the electrostatic effect. On the other hand, the adsorption enthalpy for the physical adsorption is usually in the range of nil to −42 kJ/mol, and that for the chemical adsorption is in the range of −42 to −125 kJ/mol. Hence, based on a ΔH^0 value of −19.75 kJ/mol in this study, the adsorption of 2,4,5-TCP onto BHDTMA could also be considered as a physical adsorption. In addition, the negative ΔH^0 value implies that the adsorption process is exothermic, which was in good agreement with the experimental observations. The negative value of ΔS (−21.38 J/mol) suggests that the randomness decreased in the liquid/solid interface in the adsorption of 2,4,5-TCP onto BHDTMA.

4. Conclusion

As a valuable raw material, this exchanged organoclay may have environmental applications in treating water for the removal of organic pollutants. Attention was given to chlorinated phenols because they are highly toxic.

Adsorptions of 2,4,5-TCP onto organo-bentonite (BHDTMA) were studied. The clay was modified by ionic surfactant HDTMA, which penetrated into interlamellar region of the clay by the expansion of clay sheets. This study shows that BHDTMA is a good adsorbent for the removal of 2,4,5-TCP and an effective low-cost adsorbent for the removal of this pollutant. The adsorption for the system was found to be dependent on pH, contact time and temperature. The equilibrium adsorption data of 2,4,5-TCP was best represented by the Langmuir-Freundlich isotherm. The maximum adsorbed of 2,4,5-TCP by BDTMA is 72.14 mg/g at pH 2., and temperature 20°C. Adsorption kinetics was found to follow pseudo-second-order. The negative values of ΔG^0 signify that the process of adsorption is spontaneous. The negative value of ΔH^0 (−19.75 kJ/mol) shows that the mechanism of adsorption is physical and exothermic process. The negative value of the entropy implies the decreased randomness at the solid/solution interface in the adsorption of 2,4,5-TCP onto organo-bentonite.

It may be concluded that this exchanged organoclay may have environmental applications in treating water for the removal of organic pollutants. BHDTMA is a low-cost and no pollutant natural adsorbent material.

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