Chemical Engineering Journal 146 (2009) 345–354

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Removal of 2,4-DCP from wastewater by CTAB/bentonite using one-step and two-step methods: A comparative study

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ARTICLE INFO

Article history:
Received 10 January 2008
Received in revised form 22 April 2008
Accepted 19 June 2008

Keywords:
Bentonite
CTAB
Adsorption
One step
Partition

ABSTRACT

Adsorption removal of 2,4-dichlorophenol (2,4-DCP) from aqueous solutions by bentonite/CTAB was studied using two ways: the first one using organophilic bentonite as adsorbent. This material was prepared by exchanging the organic cations as cetyltrimethylammonium bromide (CTAB) for sodium (Na^+) on the layer surface of clay (two steps method). The second way was using bentonite as adsorbent, which is in contact with simultaneous 2,4-dichlorophenol and CTAB in solution (one-step method).

This process of wastewater treatment is of interest for the stabilization of wastes in which simultaneous 2,4-DCP/surfactant contaminations occurs. This wastewater treatment was based on simultaneously synthesis of organophilic bentonite and removal of 2,4-dichlorophenol from water in one-step. Batch adsorption studies were conducted to evaluate the effect of various parameters such as the quaternary ammonium cation (CTAB) loading, contact time and initial 2,4-DCP concentration. Adsorption equilibrium reached earlier by one-step method than onto organophilic bentonite. The adsorption kinetics was tested for Elovich, intraparticle diffusion, pseudo-second-order, and pseudo-first-order reactions and rate constants of kinetic models were calculated. The equilibrium adsorption data were analysed by Freundlich, Langmuir, and Redlich–Peterson using non-linear regression technique. Freundlich isotherms best fitted the data for adsorption equilibrium for both methods. The experimental observations indicate that adsorption behaviour of 2,4-DCP is different in each case. Due to its organophilic nature, exchanged bentonite is able to adsorb 2,4-DCP at a very high extent (about 1.5 mmol/g) when the 2,4-DCP is the only solute. In the case of simultaneous presence of 2,4-dichlorophenol (2,4-DCP) and cetyltrimethylammonium bromide in solution, the adsorption capacity of 2,4-DCP strongly increases (about 2.5 mmol/g). The results indicated that the one-step process is an efficient, simple and low cost technology for removal of organic pollutants and cationic surfactants from water.

1. Introduction

Among the different pollutants of aquatic ecosystems, phenols, especially the chlorinated ones, are considered as priority pollutants since they are harmful to organisms even at ppb levels [1]. General weakness, fatigue, ataxia, headache, anorexia, sweating, hyperpyrexia, nausea, vomiting, tachycardia, abdominal pain, terminal spasms and death characterize acute poisoning by dichlorophenol. European Union (EU) has classified several phenols as priority contaminants and the 80/778/EC directive lays down a maximum concentration of 0.5 μg/L for total phenols in drinking water [2]. Chlorinated phenols with less than three chlorines are not used extensively, except in the production of higher chlorophenols and chlorophenoxyacetic acid herbicides. They have been used in many applications over the last 50 years, and especially as a fungicide and insecticide for wood preservative [3]. Environmental contamination with these chemicals occurs from industrial effluents, decolouration of paper and paper mill effluents, agricultural runoff, breakdown of chlorophenoxyacetic acid herbicides and hexachlorobenzene and from spontaneous formation following chlorination of water for disinfections and deodorization [4]. The fate of phenolic compounds in the environment and their removal from aqueous media are complicated because of their high solubility and low air–water partition coefficients.

Bentonites are argillaceous materials that can be effectively employed as adsorbents for many wastewater pollutants due to their high specific surface area. This outstanding capability is due to the presence of the mineral montmorillonite. However, their adsorption capacity for organic molecules that are highly water-soluble, polar, is very low. This is due to the hydrophilic nature of the mineral surfaces.

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doi:10.1016/j.cej.2008.06.028

However, by intercalation of long chain cationic surfactants, such as quaternary ammonium ions [R_4N^+], into the interlayer space, the natural bentonite surface properties can undergo conversion of hydrophilic to hydrophobic characteristics, resulting in modified clays having high adsorptive capacities. Such organophilic bentonite has various applications [5], and also act as adsorbents for a great variety of organic pollutants [6,7].

The traditional applications of organophilic bentonite in removal of organic pollutants from wastewater include two steps: the first is the synthesis of organophilic bentonite; the second is using this organophilic bentonite to remove pollutants from wastewater by adsorption. The synthesis process involved pulverizing bentonite and agitated mixing with surfactant solution for several hours, and then the product was centrifuged, washed several times, then dried and ground [8,9]. Large amounts of water and power were required in the process, which could be a limiting factor for the application of bentonite to wastewater treatment. In addition, it was observed that the traditional organophilic bentonite was difficult to be separated from the treated water by settlement, which posed another barrier to its industrial application [10,11]. Thus, bentonite has not been applied to the engineering of wastewater treatment because of complicated process and high cost [11]. An optimal adsorbent for the removal of organic compounds in wastewater should have the following properties: low cost, ease of handing, environmental neutrality, high affinity and high capacity.

In order to reduce the cost and simplify the process of wastewater treatment by organophilic bentonite, a one-step process including both the synthesis of organophilic bentonite and its adsorption removal of organic pollutants from wastewater was proposed in this research. In the one-step process, the adsorbate and cationic surfactants were dispersed in wastewater, and then the sodium-exchanged bentonite was added. Thus, the organic pollutants were removed from water accompanied with the synthesis of organophilic bentonite [12]. Especially, the presence of cationic surfactant in the wastewaters of pigments, dyestuffs, rubber products or agriculture chemicals manufactures, may achieve the one-step process by the addition of bentonite and simultaneously remove both the surfactants and organic pollutants [13].

Cationic surfactant in the wastewater could be utilized for the removal of organic pollutants. Thus, the process could greatly reduce the cost of water and power for synthesis of organophilic bentonite. Of all possibilities, this one-step process for bentonite application could become a simple, efficient and economically acceptable alternative to conventional physical–chemical treatment processes. Furthermore, the adsorbed organophilic bentonite could be recycled or prepare porous clay hetero-structures [11].

No detailed information about adsorption potential of bentonite from Algerian varieties has been published on bentonite behaviour in the presence of mixed 2,4-dichlorophenol/CTAB contamination. In this paper the adsorption properties of organophilic bentonite in aqueous phase and bentonite in the presence of both organic and surfactant contaminations were studied. From these aspects, our previous work was concentrated on the adsorption of the model pollutant 2,4-DCP on surfactant–clay complexes by two ways. First, the surfactant is added into the solution containing the pollutant and the complex CTAB-2,4-DCP is adsorbed onto bentonite. The second way is the sorption of the pollutant (2,4-DCP) onto bentonite exchanged with CTAB (organobentonite). The objectives of this study are:

(1) To determine the feasibility of removal 2,4-DCP by one-step method;
(2) To compare the effectiveness of one-step method with two steps one;
(3) To study the influence of parameters such as contact time, concentration of adsorbate and surfactant on the contaminant removal.

2. Experimental

2.1. Bentonite

The bentonite used in this work comes from a quarry located in Maghnia (West of Algeria) was supplied by company "ENOF" (an Algerian manufacture specialized in the production of nonferric products and useful substances). The main impurities are quartz, cristobalite and calcite. Its chemical composition was found to be as follows: 54.90% SiO_2, 1.85% MgO, 27.71% Al_2O_3, 0.08% K_2O, 0.08% CaO, 2.82% F_2O_3, 3.14% Na_2O, 9.4% loss on ignition. The cation exchange capacity (CEC) was determined with conductimetric method as 101.25 meq/100 g of bentonite. The conductimetric method was based on changed species. Ion exchanges between Mg–Ba occur by titrate the barium saturated montmorillonite suspension 1 g/100 mL with 0.02 M $MgSO_4$ solution. The plot of specific conductance against the titrant volume shows two phases. The first curve obtained with little change in conductance owing to the formation of insoluble $BaSO_4$ and the second curve, the conductance increased owing to the presence of excess magnesium ion and sulfate ion in the solution. The equivalent point is taken at the intersection of the two linear portions corresponding to the CEC [14,15].

2.2. Exchanged bentonite preparation

The organic clay was prepared by exchanging the inorganic cation of bentonite with quaternary ammonium cation at the following percentage of the clay's CEC according to the procedure described by Bartlet-Hunt et al. [16]: the quantity of organic cation added to the bentonite was determined by

$$f = \frac{M_{\text{cation}}}{\text{CEC} \times M_{\text{clay}} \times \text{GMW}_{\text{cation}} \times X} \qquad (1)$$

where f: fraction of cation exchange capacity satisfied by organic cation (dimensionless), M_{cation}: mass of organic cation required to achieve desired fraction of CEC (mass), CEC: cation exchange capacity of clay (equivalents/mass), M_{clay}: mass of clay (mass), $\text{GMW}_{\text{cation}}$: gram molecular weight of organic cation (mass/mol), and X is the moles of charge per equivalent (mole/equivalent).

Theoretically, the cation exchange capacity represents the maximum amount of organic cation that can be exchanged onto the clay's surface. The measured total organic content exchanged onto the organoclay agreed well with the calculated theoretical value [17]. The synthesis of organoclay was performed by the following procedure: 1 g of Na–bentonite was first dispersed in about 100 mL of deionised water, to which a desired amount of cetyltrimethylammonium bromide was slowly added. The concentrations of CTAB were from 17 CEC to 120 CEC of bentonite. The reaction mixtures were stirred for 24 h. All products were washed until free bromide anions (tested by $AgNO_3$), dried at 60 °C and ground in an agate mortar. The method to prepare organoclay was labelled as method for two steps.

Cetyltrimethylammonium bromide (99%), of chemical formula $C_{19}H_{42}NBr$ obtained from ACROS ORGANICS consists of a 16-carbon chain tail group attached to a trimethyl quaternary amine head group with a permanent +1 charge.

2.3. Adsorbate

The 2,4-dichlorophenol (2,4-DCP) used in this study was an analytical grade reagents of 95% purity from Sigma Chemical Co. The stock solutions were prepared in 0.1 mol/L KCl in order to promote the flocculation and to have a constant background electrolyte concentration. The properties of 2,4-dichlorophenol are given in Table 1. Due to the sensitivity of adsorption to pH fluctuations in the region near the p*K*a of the chlorophenols, as weak organic acids with a relatively high K_{ow} and p*K*a 7.83, the use of the buffer to prevent pH change was felt to be more important than the shift in adsorption capacity at a given pH due to the presence of the buffer. It was shown in a previous study that the adsorption of phenolic compounds is reduced drastically when the pH value is larger than p*K*a [18]. In this study the p*K*a value of chlorinated phenols was always greater than the pH values. Therefore the dissociation of phenolic compounds, from neutral form to phenolate form, would not be significant.

2.4. Kinetic and equilibrium experiments

The adsorption experiments were determined by using the batch equilibration technique, and were conducted in laboratory by contacting a specific volume of 2,4-DCP (adsorbate) with the same quantity of bentonite or organophilic bentonite as an adsorbent.

The effect of cetyltrimethylammonium bromide ions on 2,4-dichlorophenol adsorption was assessed through the determination of CTAB isotherm in the presence of the 2,4-DCP at 5 mmol/L concentration.

In order to evaluate kinetic data, 5 g of adsorbent was added to 1 L of known initial concentration 5 mmol/L of 2,4-DCP (organophilic bentonite alone for two step or bentonite in presence of CTAB for one step) and the mixture was allowed to agitate at an identical stirring speed of 300 rpm. In preliminary adsorption test, negligible effect of the stirring speed was observed. At given time intervals, about 2.5 mL of solution was sampled using a 10 mL-syringe, then centrifuged and the equilibrium concentrations of the adsorbate were calculated, after measuring their absorbance values at wavelength of 285 nm by UV–vis spectroscopy (SAFAS bundle of type MC^2) [19].

Isotherm experiments were carried out at 25 ± 1 °C using a water bath shaker. 50 mL of solutions of varying concentration of the 2,4-DCP from 1 to 20 mmol/L were placed in vials. An equal amount 0.25 g of organophilic bentonite was introduced into each vial, stirring for 40 min. The collected samples were then centrifuged and analysed as mentioned above.

The adsorption isotherms were carried out by shaking 0.25 g of sodium-exchanged bentonite with 50 mL of the solution containing variable initial concentration (1–20 mmol/L) in distilled water and in the presence of 5 mmol/L CTAB. After stirring for 40 min, each sample was centrifuged. The supernatant were analysed at 285 nm.

Controls containing DCP solution and no adsorbent were measured for each adsorption experiment. The controls were used to obtain a calibration curve for each measurement.

For the adsorption experiment, the mass of the chlorophenol that was lost from solution during equilibration was assumed to be adsorbed by the adsorbent:

$$q_e = \frac{(C_i - C_e) \times V}{M} \qquad (2)$$

where q_e is the mass of solute adsorbed by the adsorbent (mmol/g), C_i is the initial concentration of solute (mmol/L), C_e is the solution-phase solute concentration at the end of the adsorption experiment (mmol/L), V is the volume of solution (L), and M is the mass of the adsorbent (g).

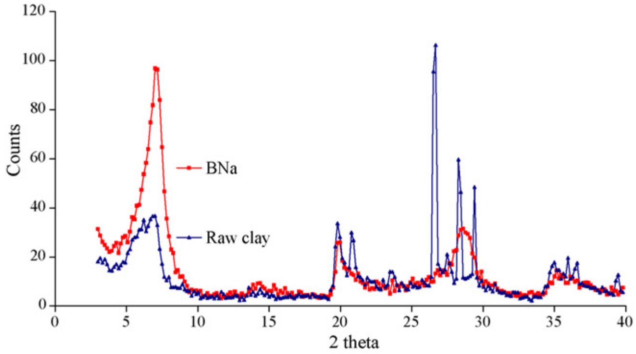

Fig. 1. X-ray diffraction of raw and sodium-exchanged bentonite.

3. Results and discussion

3.1. Characterization of bentonite

The presence of quartz and calcite impurities was detected from X-ray Diffraction (XRD) pattern in Fig. 1. Saturation of the clay by K^+ changed the diffraction from 15.65 to 12.12 Å (Table 2). It is thus a smectite. Vermiculite gave a reading of 10.5 Å after this test. The irreversible collapse of the layers of a smectite at 9.6 Å after saturation with lithium, heating overnight to 250 °C and immersion in glycerol, shows that the mineral is a montmorillonite. Saponites and swelling beidellites give a reading of 17.7 Å after this treatment. So our clay thus consists of montmorillonite [20].

The basal spacing of the bentonite is found to be 12.12 Å (Table 2). The cation exchange capacity was 101,25 meq/100 g of Bentonite and BET surface area was determined as 110,07 m^2/g in a previous paper [21].

3.2. Characterization of organophilic bentonite

Bentonite modified by large alkyl cations such as CTAB gives organophilic clay. As shown in Table 3 the CTAB cations were intercalated in the interlayer space of the bentonite and the spacing increased gradually with CTAB salt addition. When the concentration of CTAB was over the CEC of the initial bentonite, the interlayer spacing of organophilic bentonite did not increase further, our results is similar to that given by the literature [22].

The CTAB molecule is formed by a 16-carbon chain tail group with a trimethyl quaternary amine head group with a permanent +1 charge. The position of the organic molecules in the clay layer changes according to the amount of what was added [23,24]. At low addition of CTAB, equivalent to 0.35 times the CEC, the spacing was

Table 1
Selected physical and chemical characteristics of 2,4-DCP

Compound	Formula	MW (g/mol)	Water solubility (mg/L)	log K_{ow}	p*K*a
2,4-DCP	$C_6H_3Cl_2OH$	163.01	4500	3.23	7.85

Table 2
The variations of the basal distance according to tests of behaviour's clay

Samples	Raw clay	Solvatation of ethylene glycol	Saturation of K^+	Hofman Kleme test
d_{001} (Å)	15.65	17.77	12.12	9.61

Table 3
Interlayer spacing of sodium and CTAB-bentonite

CTAB concentration used in synthesizing CTAB-bentonite following percentage of the clay's CEC (% CEC)								
(% CEC)	BNa	17	34	51	68	85	100	117
d_{001} (Å)	12.12	13.76	14.34	15.44	16.44	18.34	19.87	19.02

around 14.0 Å, Table 3, indicated that one monolayer of the alkylammonium cation is accommodated in the interlayer [25]. Subsequent addition of CTAB cation into the layers led to an increase in $d_{(001)}$ spacing up to around 20 Å, Table 3.

The orientation of alkylammonium ions between silicated layers is variable. Alkylammonium ions form a monolayer (13.7 Å), a double layer (17.7 Å), a pseudo-trimoleculaire layer (21.7 Å) or a parafinic complex (>22 Å) [26]. The bentonite obtained by treatment with CTAB equivalent to 100% the CEC of initial bentonite showed high spacing of 19.87 Å (Fig. 2). This basal spacing corresponds to a bilayer of organic cations between the silicate layers (thickness about 7 Å). In aqueous systems, quaternary ammonium cations can be retained by both the outer and interlayer surfaces of clay via an ion exchange process and are not easily displaced by smaller cations as H^+, Na^+, or Ca^{2+} [27–29].

The adsorption of surfactants from water on mineral substrates is governed mainly by electrostatic and hydrophobic interactions [30] which include both the interaction between the surfactant and the surface and the mutual interaction between surfactant molecules (the main factors involved are (i) electrostatic interactions between the surfactant head group and the surface, (ii) the interaction between the tails, and (iii) the electrostatic repulsion between the head groups). Further adsorption of CTAB occurs by interaction between alkyl tails of the pre-adsorbed surfactant cations and the surfactant molecules in solution. The double layer of quaternary ammonium result in a built up of positive charge on the clay surface [27,31].

The experimental value of organic contents of the prepared organoclay (17.67%) was fairly close to 100% CEC [20]. General characteristics of the bentonite and organophilic bentonite samples are listed in Table 4.

3.3. *Effect of amount of CTAB on adsorption of 2,4-dichlorophenol by bentonite (method one step)*

The effects of CTAB were examined in more detail in the following series of experiments, in which amounts of the adsorbent and initial 2,4-DCP concentrations were kept constant, whereas the surfactant concentrations varied. The dependency of the 2,4-dichlorophenol adsorption with the concentrations of surfactant is shown in Fig. 3. As can be seen, the presence of cationic (CTAB) surfactants exhibited a rather pronounced effect on the adsorption of 2,4-DCP on bentonite. However, as CTAB concentration adds up to 5 mmol/L, the adsorption percentage of 2,4-DCP was reduced. In the presence of an excess of CTAB, the 2,4-dichlorophenol reduced dramatically. The 2,4-DCP adsorption was enhanced in the presence of low concentrations of surfactant. At high surfactant concentrations, a steep decrease in the 2,4-DCP adsorption was observed in this system, probably due to the formation of micelles that solubilise the 2,4-dichlorophenol molecules and prevent their adsorption. Adsorption isotherms of 2,4-DCP in presence of CTAB compound were investigated, with a constant CTAB concentration of 5 mmol/L.

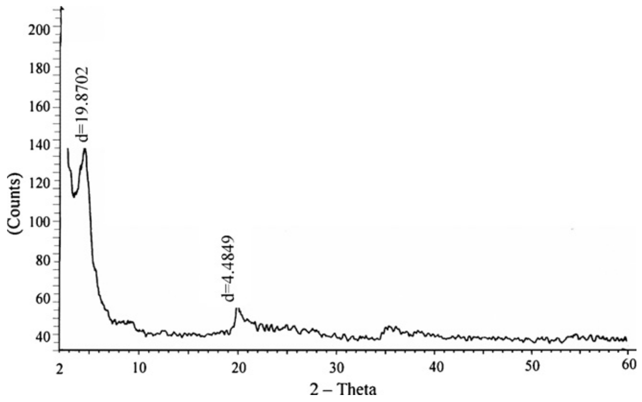

Fig. 2. XRD spectrum of the CTAB modified bentonite (100% CEC).

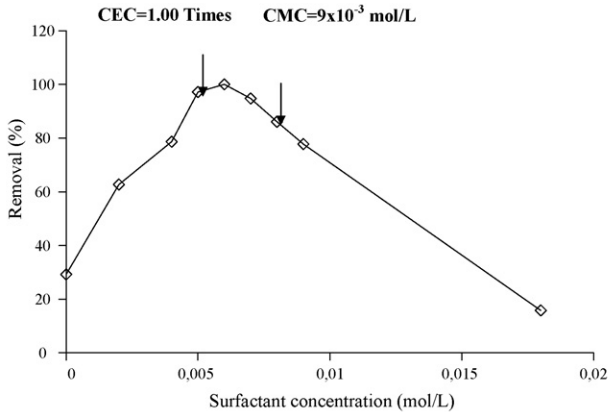

Fig. 3. Percentage removal of 2,4-DCP on bentonite from 5 mmol/L solution as function of the total quantity of surfactant (C_0, 5 mmol/L; V, 1 L; m, 5 g; pH 5).

The adsorption of 2,4-DCP on bentonite in the presence of a cationic surfactant is enhanced if surfactant has been completely adsorbed. The extent of this enhancement depends on the hydrophobicity of the clay surface. Other works [32] explain different types of adsorption depending on the extent and density of the adsorbed surfactant layer: for small concentration of cationic surfactant, adsorption of the pollutant can be assumed on simultaneous adsorption of pollutant in addition to the cationic surfactant. If the density of the adsorbed surfactant layer is large, retention of the pollutant in the surfactant film can be assumed. With amounts of surfactant higher than the CEC of the adsorbent, synergistic effects occur. These are expressed in a further enhancement of the pollutant adsorption and a simultaneous enhancement of surfactant adsorption. With increasing surfactant concentration, micelles formation is preferred to formation of a mixed film at the surface. The micelles compete with the adsorbed surfactant films for the pollutant molecules. The decrease of the adsorption amount of the

Table 4
General characteristics of Na-bentonite and surfactant-modified bentonite

Property	Sample	
	Na^+ bentonite	CTAB-bentonite
Cation formula	–	$C_{19}H_{42}N^+$
Molecular weight of cation	–	364.46
CEC (meq/100 g clay)	101.25	–
S BET (m^2/g)	110.07	–
Organic carbon content (%)	0.05	17.67

pollutant with increase in the equilibrium surfactant above its critical micelle concentration after the maximum adsorption amount has been reached, is presumably due to solubilisation of the pollutant in the micelles in the aqueous phase [33]. These phenomena had been also observed in some co adsorption studies [33,34]. It was observed that the co adsorption amount of organic solutes decreased when the surfactant concentration close to the critical micelle concentration (CMC) in the bulk phase. However, interestingly, the residue CTAB concentration was low far from CMC in this study when the adsorbed amount began to decline. Compared with the results of some adsolubilisation studies onto other particles [35,36], the adsorbed amount of CTAB was much more than those results. As the surfactant-packing amount kept on increasing, the vacancy volume in the interlayer of bentonite was not large enough to take up more molecules. The steric hindrance effects occurred. When the concentration of CTAB further increased, the free micelles were formed in the solution; the solute was incorporated in these micro reservoirs, which led to the removal efficiency of phenols continue to decrease.

3.4. Effect of amount of CTAB on adsorption of 2,4-dichlorophenol by organophilic bentonite (method two step)

Fig. 4 shows the influence of surfactant added at the percentage of the clay's CEC on the percentage removal of 2,4-DCP on organophilic bentonite. It has been reported that natural bentonite do not show adsorption capacity for chorophenols, being the contribution of physical adsorption by surface and edge groups of the silicate layers negligible [37–39]. Hence, the adsorption increment of 2,4-DCP showed by the sodium-exchanged bentonite, can be attributed to the presence of the hydrophobic sites on the surface developed by siloxane groups of the intercalated CTAB cations.

The adsorption of 2,4-DCP increases with increasing amount of intercalated CTAB until 100% of the initial CEC, has been reached. If even higher quantities of surfactant are intercalated, the adsorbed amount of 2,4-dichlorophenol decreases again significantly. This agrees well with the results found by other works [12]. The natural bentonite had little affinity for phenols in the absence of cationic surfactant, when the amount of CTAB increased, the removal efficiency increased sharply to 100%. However, the removal efficiency was not monotonically increased with the increase of CTAB amount. When CTAB amount exceeded 200% CEC, the removal efficiency decreased about 15%. The results implied that the ratio of CTAB intercalated to bentonite had a great influence on phenols removal.

To reveal the behaviour of CTAB in the adsorption, a more detailed investigation was conducted for adsorption of 2,4-DCP. As shown in Fig. 4, almost all CTAB was removed by bentonite at the amount below 200% CEC of bentonite, which suggested that CTAB was firmly anchored on negatively charged bentonite in that range. The CTAB was anchored by cationic exchange [12]. When the cationic exchange exceeded 100% CEC, CTAB was adsorbed. Van der Waals hydrophobic interactions were suggested to operate in such cases and lead to a bilayer of interdigitated alkyl chains [25]. In consequence, the admicelles, hemimicelles, or other aggregated surfactant states formed an effective medium (i.e., a solvent-like phase) for solute partitioning, which greatly enhanced the phenols uptake and more surfactants were adsorbed.

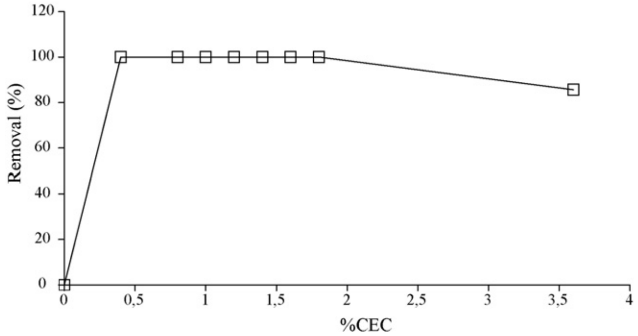

Fig. 4. Percentage removal of 2,4-DCP onto bentonite exchanged with CTAB cations at the percentage of the clay's CEC (C_0, 5 mmol/L; V, 1 L; M, 5 g; pH 5).

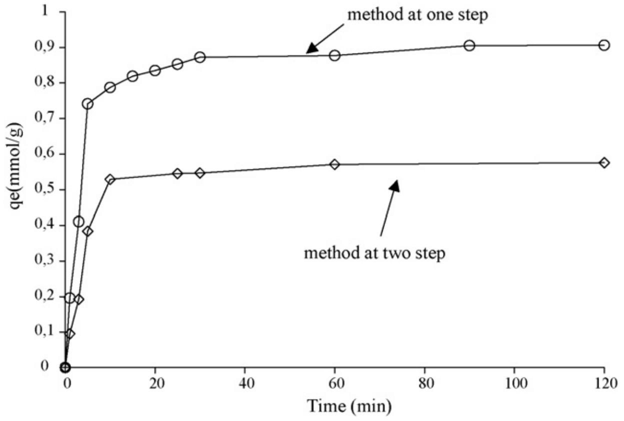

Fig. 5. Adsorption kinetics for 2,4-DCP by two methods (C_0, 5 mmol/L; V, 1 L; M, 5 g; pH 5).

From this results, we tried to compare the kinetic and the isotherm for the adsorption of 2,4-DCP by two methods: first by organophilic bentonite (CTAB exchanged bentonite at 100% CEC labelled method at two step) and by sodium-exchanged bentonite in the presence of mixed 2,4-dichlorophenol and constant concentration 5 mmol/L of CTAB (method labelled method at one step).

3.5. Adsorption kinetics experiments

Fig. 5 shows the plot of the amount of 2,4-DCP adsorbed (mmol/g) against contact time at initial concentration of 5 mmol/L by bentonite in presence of CTAB in solution (one-step method) and by organophilic bentonite (two-step method). The kinetic curves show that the equilibrium time and adsorption capacity of bentonite in presence of CTAB in solution and organophilic bentonite are quite different. Using bentonite in one-step method as adsorbent, the removed amount of 2,4-DCP presents a faster initial step (5 min) and after that it increases slowly until approximately 30 min. The amount of adsorbed 2,4-DCP was 0.857 mmol/g. For organophilic bentonite, only 10 min were necessary for reaching equilibrium and the maximum amount of adsorbed 2,4-DCP was 0.528 mmol/g. The rate of adsorption of 2,4-DCP was found to be 0.1945 and 0.098 mmol/g min^{-1} by one step and two steps respectively. Between 5 and 30 min the rate of adsorption of 2,4-DCP decreased with bentonite in presence of CTAB in solution, given 0.0320 mmol/g min^{-1} and organophilic bentonite, given 0.0216 mmol/g min^{-1} for 5 mmol/L of 2,4-DCP concentrations. Above 60 min the rate of 2,4-DCP decreased, given 1.462×10^{-2} mmol/g min^{-1} by one step and 9.506×10^{3} mmol/g min^{-1} by two steps. However, a prediction of the effects of surfactants on adsorption is not easy, as several simultaneous and competitive mechanisms may be operating during the adsorption process. To explain complicated effects of surfactants on the adsorption of 2,4-DCP onto bentonite, the following mechanisms were considered:

The slow adsorption of 2,4-DCP onto organophilic bentonite may be explained by the fact that the surfactant is initially exchanged in bentonite. So, the removal of the pollutant is rapid when CTAB is present in solution. In this case, adsorption of the pollutant can be assumed on simultaneous adsorption of pollutant in addition to the cationic surfactant. When the density of the adsorbed surfactant layer is large, an adsolubilisation of the pollutant in the surfactant film can be assumed.

The increased adsorption capacity of bentonite treated with cetyltrimethylammonium ions for 2,4-DCP is due to the alkyl chains in the interlamellar spaces. The adsorption on organophilic bentonite may occur via different mechanisms or additional mechanisms, because the resultant organoclay (CTAB exchanged bentonite) have low surface areas and act as partitioning media in the sorption [39].

Three consecutive mass transport steps are associated with the adsorption of solute from solution by porous adsorbent [40]. First, the adsorbate migrated thought the solution to the external surface of the adsorbent particles by molecular diffusion, i.e., film diffusion, followed by solute movement from the particles surface into internal sites by pore diffusion and finally the adsorbate is adsorbed onto active sites at the interior of the adsorbent particles. This phenomenon takes relatively long contact time.

In order to study the rate-determining step for the adsorption of 2,4-DCP, the pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion kinetic models are analysed. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2). A relatively high R^2 value indicates that the model successfully describes the kinetics of 2,4-DCP adsorption.

The pseudo-first-order kinetic equation in the following form can be used [41].

$$\log(q_e - q_t) = \log q_e - \frac{k_1 \times t}{2.303} \tag{3}$$

where q_t and q_e represent the amount of 2,4-DCP adsorbed (mmol/g) at any time t and at equilibrium time, respectively, and k_1 represents the rate constant of pseudo-first-order adsorption (min^{-1}).

A pseudo-second-order equation based on adsorption capacity may be expressed in the following form [42]:

$$\frac{t}{q} = \frac{1}{k_2 \times q_e^2} + \left(\frac{1}{q_e}\right) \times t \tag{4}$$

where k_2 is the rate constant of pseudo-second-order adsorption (g/(mmol min)) and q_e is the amount of 2,4-DCP adsorbed at equilibrium (mmol/g).

The kinetics of adsorption of 2,4-DCP was also examined using Elovich equation [43] in the following form:

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \tag{5}$$

where α is the initial adsorption rate (mmol/g min), β is the desorption constant (g/mmol) during any one experiment. The Elovich coefficient could be computed from the plots of q_t vs. $\ln t$.

Fig. 6 shows the linearised form of the pseudo-first-order and pseudo-second-order kinetic for adsorption of 2,4-DCP by two methods (one and two step). The rate constants k_1 and k_2 obtained from the plots of Eqs. (3) and (4) are shown in Table 5. Pseudo-first-order model only achieved a good fitting for the first minutes of experimental data. The best fits, in the whole data range, were found with the pseudo-second-order model, indicating that the rate-limiting step is a chemical adsorption process between 2,4-DCP and organophilic bentonite and bentonite in the presence of CTAB in the same solution of 2,4-DCP. Similar conclusions were found by Ho and McKay as a result of an analysis of data from the literature. They reported that the most of the adsorption systems follow a pseudo-second-order kinetic model [42]. From Table 5, it is interesting to note that the initial adsorption rate of 2,4-DCP onto adsorbents by two methods had the following tendency: one step > two step. Also adsorption of 2,4-DCP by one step had a higher adsorption capacity towards two steps, and exhibited faster kinetics. This implies that a stronger interaction may occur between 2,4-DCP and some active sites of the same activity than with other sites on the organophilic bentonite surface. The reactivity might be related to the presence of CTAB in solution. For chemisorptions on highly heterogeneous adsorbents, the Elovich equation sometimes gives a better account of the second-order kinetics. The plot of the Elovich equation for the experimental data was obtained with correlation coefficients between 0.78 and 0.83 (results not shown). These values are lower than those of the pseudo-second-order equation. The Elovich equation does not predict any definite mechanism, but it is useful in describing adsorption on highly heterogeneous adsorbents [44–46]. Similar trend was observed by O¨zacar et al. [47] for the adsorption of lead onto valonia tannin resin.

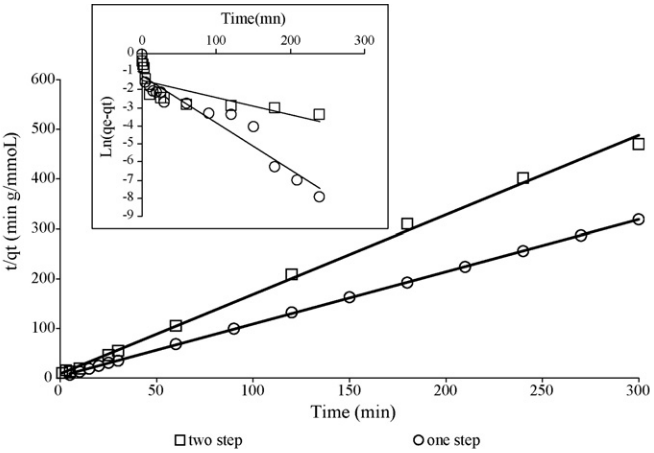

Fig. 6. Pseudo-second-order kinetics for adsorption of 2,4-DCP on bentonite by one step and two step. Inset, pseudo-first-order kinetics for adsorption of 2,4-DCP on bentonite by two different methods (C_0, 5 mmol/L; V, 1 L; M, 5 g; pH 5).

The intraparticle diffusion model was tested in this work. The intraparticle diffusion originates from Fick's second law. Weber and Morris stated that if intraparticle diffusion is the rate-controlling factor, uptake of the adsorbate varies with the square root of time [48]. Thus, rates of adsorption are usually measured by determining the adsorption capacity of the adsorbent as a function of the square root of time [49]. Ho and Mc Kay [50] have shown that it is essential for the q_t vs. $\sqrt{t}$ plots to go through the origin if the intraparticle diffusion is the sole rate-limiting step. When the plots

Table 5
Kinetics constants for removal 2,4-DCP by one step and two steps (C_0, 5 mmol/L; V, 1 L; M, 5 g; pH 5)

Method				
Pseudo-first-order	k_1 (min^{-1})		q_e (mmol/g)	R^2
One step	0.025		0.28	0.92
Two step	–		–	–
Pseudo-second-order	k_2 (g/mmol min)	q_e (mmol/g)	h (mmol/g min)	R^2
One step	0.323	0.95	0.292	1.00
Two step	0.284	0.63	0.113	0.99
Intraparticle-diffusion		k_P (mmol/g min$^{0.5}$)		R^2
One step		0.0103		0.90
Two step		0.0062		0.92

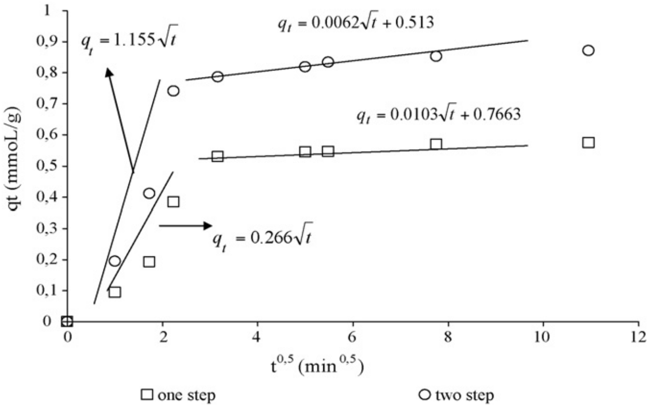

Fig. 7. Intraparticle diffusion plot for adsorption of 2,4-DCP by one step and two steps methods (C_0, 5 mmol/L; V, 1 L; M, 5 g; pH 5).

do not pass through the origin, this is indicative of some degree of boundary layer control and this further indicates that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. Since this was also not the case in the present work, it may be concluded that surface adsorption and intraparticle diffusion were concurrently operating.

According to Weber et al. [48], an intraparticle diffusion coefficient k_p is defined by the equation:

$$q_t = k_p \times \sqrt{t} \qquad (6)$$

where k_p is the intraparticle diffusion rate constant (mmol/g min$^{0.5}$), can be obtained from the slope of the plot of q_t (mmol/g) versus $\sqrt{t}$ (min$^{0.5}$).

From Fig. 7 it was noted that the adsorption process tends to be followed by two phases. The slower of two-step controls the overall rate process. Generally, intraparticle diffusion is the rate-limiting step in batch process, the correlation coefficients of intraparticle diffusion model are given in Table 5 for the adsorption of 2,4-DCP by one and two steps and although all high (>0.850), they are significantly lower than that of the pseudo-second-order kinetic model. It was found that the linear portion ended with a smooth curve followed by a linear portion. The two phases in the intraparticle diffusion plot suggest that the sorption process proceeds by surface sorption and intraparticle diffusion. The initial curved portion of the plot indicates a boundary layer effect while the second linear portion is due to intraparticle or pore diffusion. A similar type of pattern was reported previously by Sankar et al. [51] for acid and direct dye onto rice bran-activated carbon and also by Sivaraj et al. [52] for acid violet onto orange peel. The slope of the second linear portion of the plot has been defined as the intraparticle diffusion parameter k_p (mmol/g min$^{0.5}$) and the intercept of the plot reflects the boundary layer effect. The larger the intercept is the greater the contribution of the surface sorption in the rate-limiting step. The calculated intraparticle diffusion coefficient k_p value was given as 0.0062, 0.0103 mmol/g min$^{0.5}$ for organophilic bentonite and bentonite with presence of CTAB respectively.

3.6. Adsorption isotherm experiments

The adsorption of a substance from one phase to the surface of another in a specific system leads to a thermodynamically defined distribution of that substance between the phases as the system reaches equilibrium. This distribution can be expressed in terms of adsorption isotherms [53].

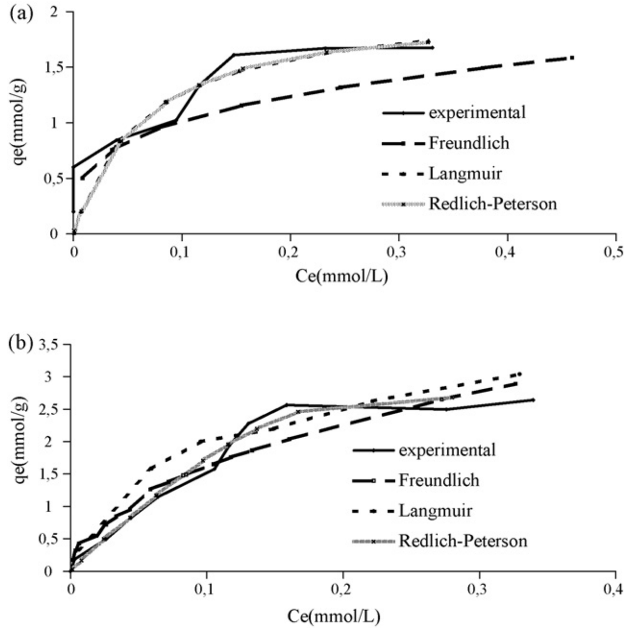

Fig. 8. Adsorption isotherms of 2,4-DCP described by the Langmuir, Freundlich and Redlich–Peterson models for (a) 2,4-DCP alone by organophilic bentonite and (b) 2,4-DCP with presence of CTAB in solution by bentonite.

The adsorption isotherms of 2,4-dichlorophenol on bentonite in the presence of CTAB and on organophilic bentonite are compared in Fig. 8(a and b). The experiments for 2,4-DCP adsorption by the two methods lead different results, as shown in Fig. 8(a and b). The comparison of plots, make clear that the presence of CTAB in solution makes the 2,4-DCP isotherm change. It dramatically increases the adsorption capacity of 2,4-DCP. According to the classification by Giles et al. [54] based on the initial slope and the shape of the upper part of the curve, the results of the adsorption experiments of 2,4-DCP on bentonite in the presence of CTAB (one-step method) shown that adsorption isotherm is of class L (Langmuir), subgroup 4. It is a multilayer type isotherm, typical of those obtained by moderate interaction between the organic compound and the bentonite, followed by a cooperative effect of the adsorbed molecules in the multilayer adsorption [55]. The isotherm is very different from the case of the adsorption of 2,4-DCP alone on organophilic bentonite. The result turn to type L subgroup 2 (Langmuir monolayer), and the formation of the monolayer takes place at the same equilibrium concentration in both cases. The low adsorbent uptake of 2,4-DCP concentrations in presence of CTAB up to about 0.05 mmol/L makes evident those solute adsorbent interactions are quite weak at low concentrations. Then, as this concentration increases, cooperative adsorption takes place to a much greater extent and brings the total adsorption capacity of about 2.5 mmol of 2,4-DCP per gram of bentonite in the presence of CTAB in solution. In the latter case interactions occur between alkyl ammonium and bentonite, but, once a CTAB molecule is adsorbed, adsorbent–CTAB interactions promote the adsorption in cooperative fashion. However, the adsorption capacity reaches values as low as about 1.5 mmol of 2.4 DCP/g of organophilic bentonite. 2,4-DCP is weakly adsorbed by bentonite [56]. The reason is that water is preferentially adsorbed. There are two types of interaction between polar organic compounds (NOCs) and organobentonites, adsorption and partition, associated with the interfacial behaviour of organic compounds in the system organobentonite/water, and is related to the organic matter and mineral surface, respectively, of the medium. Surface adsorption may include ion exchange, protonation, hydrogen bonding, and coordination/ion-dipole reactions with clays [57,58]. Partition involves interactions between organic matter and NOCs. When a large organic molecule, for example HDTMAB, interacts with bentonite, the partition process plays an important role. Chlorophenol adsorption in soil has been described assuming hydrophobic partitioning of the neutral species to soil organic matter [59] or as described by He et al. [60] as a hole-filling adsorption mechanism into the soil organic matter, facilitated by H-bonding. Resulting from the organic ion exchange the hydrophilic ions in the interlayer are replaced, and the smectite becomes generally hydrophobic. Organophilic smectites are used as an adsorbent of organic pollutants. It is proposed to regard the organophilic interlayer as an organic solvent [6,8,61,62].

The adsorption data obtained from these isotherms were analysed with respect to the Freundlich and Langmuir isotherm equations. Freundlich developed an empirical equation to describe the adsorption process [63]. His development was based on the assumption that the adsorbent had a heterogeneous surface composed of different classes of adsorption sites, with adsorption on each class of sites following the Langmuir isotherm. Freundlich [63] demonstrated that the ratio of the amount of solute adsorbed onto a given mass of an adsorbent to the concentration of the solute in the solution was not constant at different solution concentrations. This isotherm does not predict any saturation of the adsorbent by the adsorbate; thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption of the surface [64]. The Freundlich isotherm assumes that if the concentration of solute in the solution at equilibrium, C_e, is raised to the power n, the amount of solute adsorbed being q_e, then C_e^n is constant at a given temperature.

The Freundlich adsorption isotherm can be written as:

$$q_e = k_f C_e^n \tag{7}$$

where k_f is adsorption capacity at unit concentration, and n is adsorption intensity. n values indicate the type of isotherm to be irreversible ($n = 0$), favourable ($0 < n < 1$), unfavourable ($n > 1$) [65]. Eq. (7) can be rearranged to a linear form:

$$\log q_e = \log k_f + (n) \log C_e \tag{8}$$

The Langmuir isotherm equation [66] initially derived from kinetic studies is based on the assumption that on the adsorbent surface there is a definite and energetically equivalent number of adsorption sites, at each of which one molecule of a perfect molecule may be adsorbed. Langmuir adsorption model serves to estimate the maximum uptake values where they cannot be reached in the experiments. It is based on the physical hypothesis that the maximum adsorption capacity consists of a monolayer adsorption, and that there are no interactions between adsorbed molecules. The adsorption energy is distributed homogeneously over the entire coverage surface. Langmuir's equation is

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \tag{9}$$

where b is the equilibrium adsorption coefficient (L/mg) and $q_{\max}$ the maximum adsorption capacity (mmol/g), C_e the equilibrium concentration (mmol/L), q_e is the amount adsorbed at equilibrium (mmol/g). The linear form of Eq. (9) is:

$$\frac{C_e}{q_e} = \frac{1}{b q_{\max}} + \frac{C_e}{q_{\max}} \tag{10}$$

Table 6
Freundlich, Langmuir and Redlich–Peterson isotherm constants for the adsorption of 2,4-dichlorophenol by one step and two steps methods

Method	Fitted equation	$q_{\max}$ (mmol/g)	b (L/g)	R^2
Langmuir constants				
One step	$q_e = (50.249C_e/1 + 14.17C_e)$	3.546	14.170	0.984
Two steps	$q_e = (24.746C_e/1 + 10.792C_e)$	2.293	10.792	0.951
Method	Fitted equation	k_f (mmol/g)	n	R^2
Freundlich constants				
One step	$q_e = 5.173C_e^{0.51}$	5.173	0.515	0.999
Two steps	$q_e = 2.541C_e^{0.32}$	2.541	0.329	0.999
Method	k_R	a_R	β	R^2
Redlich–Peterson constants				
One step	0.905	20.687	2.418	0.801
Two steps	1.953	13.984	1.080	0.876

The Redlich–Peterson isotherm model combines elements from both the Langmuir and Freundlich equations, where the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption [67]. The Redlich–Peterson equation is widely used as a compromise between Langmuir and Freundlich systems. It is expressed by: Eq. (11):

$$q_e = \frac{k_R C_e}{1 + a_R C_e^{\beta}} \tag{11}$$

k_R and a_R are the Redlich–Peterson isotherm constants and β is the exponent, which lies between 0 and 1. The Redlich–Peterson isotherm incorporates three parameters and can be applied either in homogenous or heterogeneous systems. Eq. (11) can be converted to a linear form by taking logarithms of both the sides as Eq. (12).

$$\ln \left(k_R \frac{C_e}{q_e} - 1 \right) = \ln a_R + \beta \ln C_e \tag{12}$$

The experimental data fitted to Langmuir, Freundlich and Redlich–Peterson isotherm equation are shown in Fig. 8. The adjustable parameters ($q_{\max}$, b, k_f, n, k_R, a_R, and β) obtained are listed in Table 6. The Freundlich model exhibits better fits than the Langmuir and Redlich models. According to the coefficient of correlation obtained. The Langmuir and Redlich–Peterson isotherms are not adequate for modelling the adsorption of 2,4-DCP on bentonite by both methods. Freundlich model present good fit to the experimental data (Table 6, Fig. 8), and is adequate for modelling the isotherm of adsorption. The Freundlich exponent n gives information about surface heterogeneity and surface affinity for the solute. The Freundlich exponent n between 0.515 and 0.329 indicates favourable adsorption. Since the degree of favourability increases as n approaches zero, both of the methods show a very high affinity for 2,4-DCP. Values of $q_{\max}$, which is defined as the maximum capacity of adsorbent, have been calculated from the Langmuir plots. The maximum capacities of organophilic bentonite and bentonite for 2,4-DCP alone and with CTAB in same solution are 2.293 and 3.546 mmol/g respectively.

Table 7
Comparison of the maximum 2,4-dichlorophenol uptake capacities of various adsorbents

Adsorbent	$q_{\max}$	References
Activated carbon fiber	370 mg/g	[68]
Static-air-activated carbon fibers	400 mg/g	[69]
Allophanic soil	2400 μmol/kg	[70]
Palm pith carbon	19.16 mg/g	[19]
Granular activated carbon:	250 mg/g	[71]
Immobilized white-rot fungus Phanerochaete chrysosporium	7.15 mg/g	[72]
Organically modified layered hexaniobate $K_4Nb_6O_{17}$	2.5 mmol/g	[73]
Anaerobic granular sludge	1.6 mg/g	[74]
Phanerochaete chrysosporium biomass	12 mg/g	[75]

Table 7 shows a comparison of the maximum uptake of 2,4-DCP by the two different methods with different adsorbents found in literature. As can be seen, the removal capacity by one-step method is considerably higher than that exhibited by many of the adsorbents commonly used in many practical phenol recovery applications. More extensive compilations of the adsorption of 2,4-DCP by different materials can be found in the literature.

4. Conclusion

This paper deals with the removal of 2,4-DCP from aqueous solution by two ways; first organobentonite which is a simple bentonite exchanged at 100% CEC with CTAB and the second way is the adsorption of the pollutant and CTAB by bentonite (one step). The results of this study indicate that the method of one step improves greatly the adsorption behaviour of 2,4-DCP. The results showed that organic pollutants such as 2,4-DCP and CTAB could be simultaneously and quickly removed from water by bentonite.

Batch kinetic studies performed by organobentonite and bentonite/CTAB systems indicated that adsorption capacity by the two methods and kinetics data tended to fit well the second-order model. The intraparticle diffusion is not the only rate-limiting step; the surface adsorption and intraparticle diffusion were concurrently operating during the 2,4-DCP and CTAB-bentonite interaction. The isotherms in CTAB solutions exhibit L4 multilayer cooperative model, which increases on increasing 2,4-DCP concentration. Interactions of adsorbent–adsorbate and adsorbate–adsorbate (solute–solute) type are responsible for this behaviour.

The findings of this study were useful in determining optimum conditions for 2,4-DCP removal both from water on organophilic bentonite, and in the presence of cationic surfactant CTAB.

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