



Equilibrium, kinetics and thermodynamic studies for sorption of chlorobenzenes on CTMAB modified bentonite and kaolinite

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ABSTRACT

The sorption of chlorobenzenes (CBs) by cetyltrimethylammonium bromide (CTMAB) modified bentonite and kaolinite was investigated. The sorption isotherms for CBs were nearly linear, suggesting that sorption could be described by a distribution process. The distribution coefficient (K_d) was primarily affected by the amount of sorbed surfactant. The organic carbon normalized sorption coefficient (K_{oc}), however, was particularly dependent on arrangement of the surfactant cations. The K_d of CBs was larger for CTMAB-bentonites than that for CTMAB-kaolinites, while the case for K_{oc} was opposite. Thus, the clay mineral structure and morphology had a considerable influence on the surfactant arrangement, which was responsible for the partitioning of CBs. The sorption of CBs onto both CTMAB-bentonites and CTMAB-kaolinites followed pseudo-second-order kinetics. The intra-particle diffusion model for sorption was also investigated and compared to identify sorption mechanism. The sorption of CBs both on CTMAB-bentonites and CTMAB-kaolinites was exothermic in nature and accompanied by an increase in entropy and a decrease in Gibbs energy in the temperature range of 15–35 °C. The results indicated that CBs strongly interacted with CTMAB modified bentonite and kaolinite.

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1. Introduction

The widespread occurrence of hydrophobic organic contaminants (HOCs) in soils and groundwater has led to intensive studies of their mobility, remediation and ultimate fate [1–6]. Cationic surfactants have been shown in many instances to significantly enhance the sorption capacity of oppositely charged soil constituents for HOCs [7–10]. The increasing sorption of contaminant reduces the transport potential of mobile species, which suggests the use of this soil modification approach for in situ remediation of contaminated soils and aquifers. The feasibility of underground injection of quaternary ammonium compounds (QAC) to create a sorption zone that would intercept an advancing contaminant plume and immobilize organic contaminants therein has been demonstrated. Coupling enhanced contaminant immobilization with subsequent biodegradation within the sorption zone may provide a comprehensive in situ remediation [11]. The remediation approach is based on the fact that the inorganic exchangeable cations of naturally occurring layer silicate clays can be readily replaced by cationic surfactants such as QAC. This results in organoclays with greatly increased capabilities to remove HOCs from aqueous solution. The increasing HOC sorption in the fashion has

been demonstrated for both QAC modified clays and soils, offering a means to substantially reduce the transport potential of contaminants through engineered clay barriers, soil profiles and aquifers.

To make effective use of cationic surfactants for HOCs, however, it may be important to understand how the sorption capacity of surfactant-modified clays in soils and aquifers are influenced by temperature, time and different clay types. Some literatures indicate that surfactant treatment of soil materials is very effective in increasing their capacity for retaining HOCs [12–14]. However, to our knowledge, little work has been reported to examine the mechanism of surfactant-modified soil materials to sorbed HOCs by the kinetic and thermodynamic process.

In this study, bentonite and kaolinite were selected because they are typical clay constituents of soils and aquifers. The objectives of this study are (1) to evaluate the influence of clay type and the changes in extent of surfactant surface coverage on the sorption of CBs; (2) to examine the mechanism of CBs sorption in the kinetics and thermodynamics view; (3) it is critical to design effective, safe and economical environmental technologies using surfactant-coated materials.

2. Materials and methods

2.1. Chemicals and clays

Bentonite and kaolinite were obtained from Guangdong Corporation of Geo-Exploration & Mineral Development. The

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Table 1
Selected physicochemical properties of the chemicals used in sorption experiments [15].

Chemical	Abbreviation	MW (g/mol)	T_m ($^{\circ}$ C)	Density (g/cm ³)	log(K_{ow})	S_w (mg/L)
Chlorobenzene	CB	112.6	-45.2	1.11	2.78	458.3
1,4-Dichlorobenzene	DCB	147.2	53.1	1.25	3.45	73.6
1,2,4-Trichlorobenzene	TCB	181.5	17.0	1.45	4.06	30.1
1,2,4,5-Tetrachlorobenzene	TeCB	215.9	140.0	1.86	4.72	1.27

cation-exchange capacities (CECs) were 58.5 and 3.0 mequiv./100 g, respectively. CBs were purchased from Aldrich Chemical Co. with purity greater than 99%. The selected physicochemical properties of these chemicals are given in Table 1. Cetyltrimethylammonium bromide (CTMAB) and other reagents used were of analytical grade and obtained from Sinopharm Group Chemical Reagent Co., Ltd.

2.2. Preparation of organoclays

CTMAB-bentonites and CTMAB-kaolinities were synthesized by cation exchange. CTMAB in amounts equivalent to various percentages of the CECs (30%, 50%, 70% and 100%) was dissolved in 200 mL distilled water. A total of 40 g bentonite or kaolinite was added to the CTMAB solution at 25 $^{\circ}$ C. The dispersions were stirred for 24 h at 25 $^{\circ}$ C. The treated clays were separated from water by vacuum filtration and washed several times by distilled water until that Br⁻ in filtrate was not detected by AgSO₄ solution. The separated organoclays were dried at 80–90 $^{\circ}$ C, activated for 1 h at 105 $^{\circ}$ C, and then mechanically grinded to less than 100 mesh. The derivatives are referred to as 0.3 CEC, 0.5 CEC, 0.7 CEC and 1.0 CEC for CTMAB modified clays at 30%, 50%, 70% and 100% of CEC of the clays, respectively.

2.3. Sorption experiments

The amount of sorbed CBs was measured as a function of time, temperature and concentration by the batch technique. A known

mass of sorbent was immersed in CBs solutions of the same concentration in the case of kinetic experiments, and in solutions of different concentrations for determining the sorption isotherms, and with sorption isotherms at different temperatures for thermodynamics tests.

Sorption isotherms were obtained by batch technique at 25 $^{\circ}$ C in 20 mL glass centrifuge tubes with Teflon-lined caps. A total of 0.2 g of original clays or organoclays, followed by stock solution of CBs containing 0.01 M NaCl, was added to the vials. Test solutes stock solutions were prepared in methanol solutions, final methanol concentrations were less than 0.1% (v/v) to avoid co-solvent effects [16]. Reactors were capped immediately after stock solution added and then tumbled on a reciprocation shaker at 150 rpm for equilibrium. At determination, each reactor was then centrifuged, and an aliquot of supernatant was removed. The solute was separated by liquid/liquid extraction with hexane and analyzed by gas chromatography (Hewlett Packard 6890 plus) employed an electrolytic conductivity detector. Mass in the water phase was thus obtained, and mass sorbed was calculated by mass balance. The overall mass loss was small (<5%), and thus ignored. All isotherm experiments were performed in duplicate.

For the thermodynamic studies, similar procedure was adopted except that the temperature was varied for each isotherm.

The kinetics of the sorption process was studied by carrying out a separate set of experiments with constant temperature, clay amount and initial CBs concentrations. Each reactor was withdrawn at suitable time intervals.

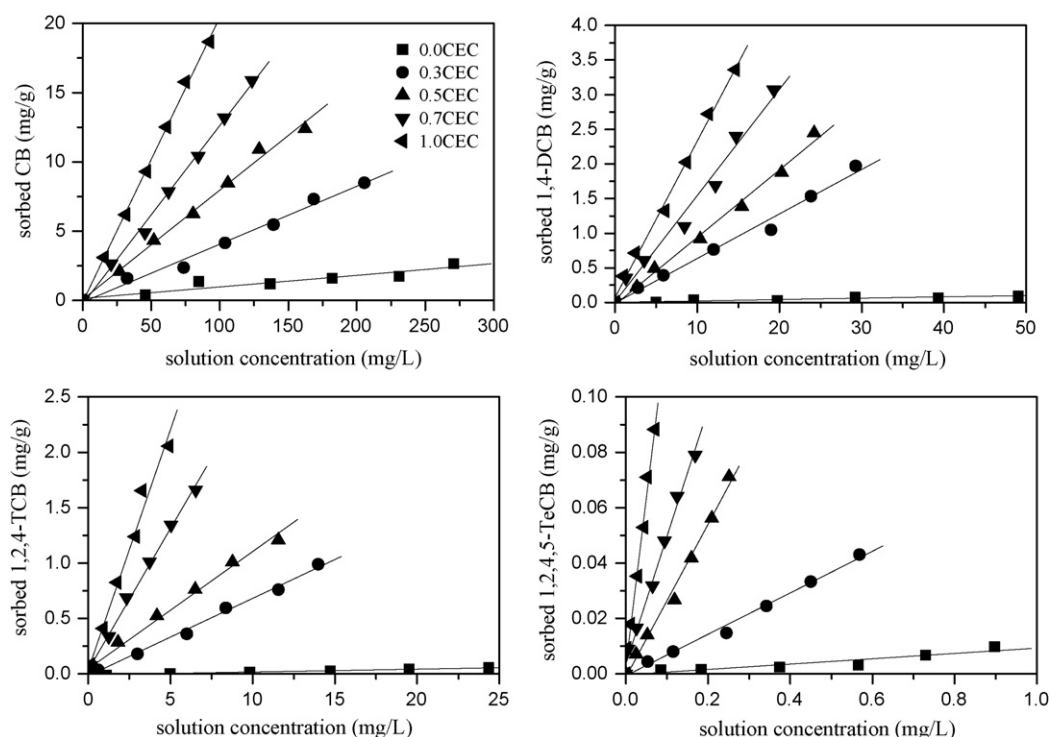


Fig. 1. Sorption of CBs by bentonite with various CTMAB surface coverages.

3. Results and discussion

3.1. Sorption isotherms

The sorption of CBs by modified bentonite with various CTMAB surface coverages is shown in Fig. 1. CBs partitioning behavior is linear at each CTMAB loading level over the range of CBs concentrations. Linear sorption of HOCs was also observed on surfactant-modified smectite and halloysite [9,17]. Similar linear behavior was also observed for CBs partitioning into CTMAB-coated kaolinites (Fig. 2). The sorption of CBs can be described by

$$C_s = K_d C_e \quad (1)$$

where C_s is the amount of sorbed CBs per unit mass of sorbent, C_e is the equilibrium concentration of CBs, and K_d is the sorption (distribution) coefficient. K_d can be normalized by the organic carbon content of the sorbent:

$$K_{oc} = \frac{K_d}{f_{oc}} \quad (2)$$

where K_{oc} is the organic carbon normalized sorption coefficient and f_{oc} is the mass fraction of carbon in the sorbent. The values of K_d , f_{oc} , K_{oc} and the sample correlation coefficients for the linear CBs sorption isotherms are presented in Table 2.

These isotherms in Figs. 1 and 2 illustrate important characteristics. The original bentonite and kaolinite sorption isotherms describe the sorption of CBs to the clays that have not been amended with CTMAB. As evidenced by the data, sorption to the original clays is almost negligible. The hydrated mineral surface of the clay prevents CBs sorption and the low organic carbon content of the clay results in negligible solute uptake by partition. By contrast, the addition of a relatively small amount of CTMAB causes a dramatic increase in the uptake of CBs relative to the untreated clays. These results encourage the continued investigation into the feasibility of the treatment of soils, aquifers and clay materials with QACs for in situ remediation, slurry wall and as liners at waste disposal sites.

Table 2 shows that K_{oc} for CBs partitioning into CTMAB-coated bentonites and kaolinites is constant over the range of coverage examined, indicating that the relative affinity of CTMAB-coated bentonites and kaolinites for CBs does not change with changing CTMAB coverage. Moreover, the data in Table 2 show that the values of K_{oc} for CBs partitioning into both CTMAB-bentonites and CTMAB-kaolinites are several times greater than those that have been reported for CBs partitioning into natural organic matter [18]. This means that a coating of CTMAB can immobilize more CBs than that would be immobilized by an equivalent coating, by weight, of natural organic matter, which is very significant for in situ remediation of CBs contaminated soils and aquifers.

The K_d values for CBs sorption on CTMAB-bentonites are generally higher than those of CTMAB-kaolinites (Table 2). However, if f_{oc} values, which are based on the amount of sorbed CTMAB, are used, K_{oc} values for CTMAB-kaolinites are larger than those of CTMAB-bentonites. This suggests that the efficiency of CBs partitioning into CTMAB-kaolinites is higher than CTMAB-bentonites, which strongly depended on the CTMAB configuration in clays. The surfactant binding mechanism may influence the sorption properties of organoclays. Bentonite is a kind of swelling layer silicates and kaolinite is a nonswelling one. On all the tested nonswelling clay surfaces, surfactants always adopt a vertical (paraffin type) arrangement. The sorbed organic cations in swelling clays such as bentonite may adopt very loose and disordered flat-lying arrangement in the clay interlayers in wet state [9,19]. This implies that kaolinite could have a more stabilized or ordered CTMAB sorption layer than bentonite. As a result, CTMAB-kaolinites showed an advantage for CBs sorption than CTMAB-bentonites, which can be seen from the larger K_{oc} for CBs partitioning into CTMAB-kaolinites than CTMAB-bentonites.

3.2. Sorption kinetics

Fig. 3 illustrates the effect of contact time on the sorption of CBs onto CTMAB modified bentonite and kaolinite. Two simplified kinetics models including pseudo-first-order and pseudo-second-

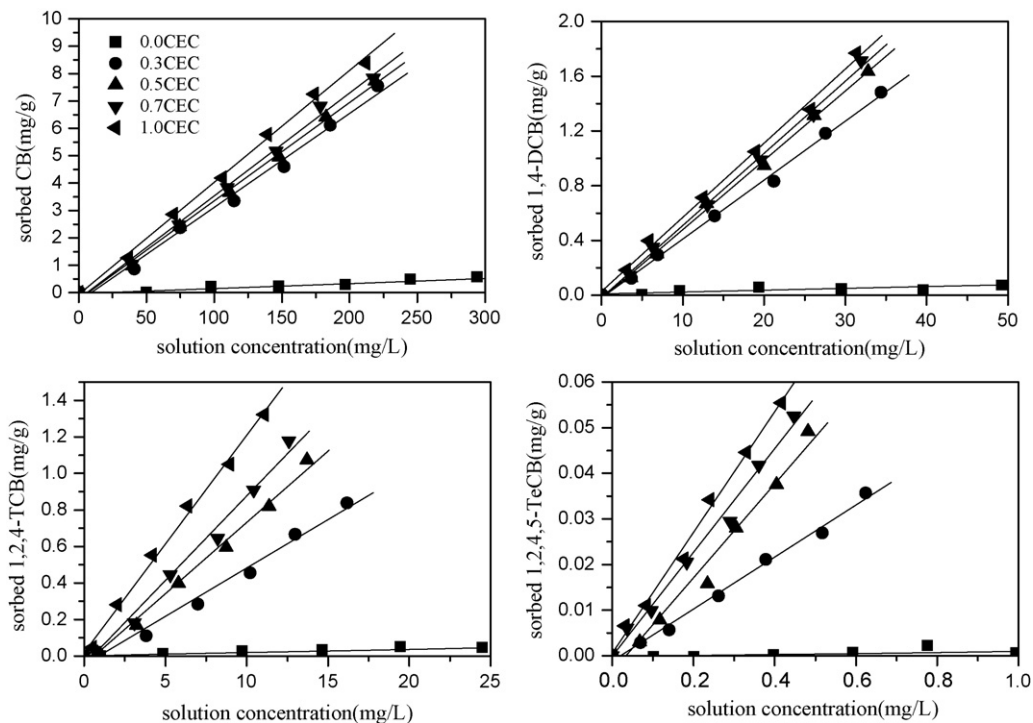


Fig. 2. Sorption of CBs by kaolinite with various CTMAB surface coverages.

Table 2
Linear isotherm parameters, organic carbon contents, and regression correlation coefficients for CBs sorption to organoclay sorbents.

Solutes	Sorbents	K_d (kg/L)	Correlation coefficient	f_{oc} (%)	K_{oc}	
CB	CTMAB-kaolinites	Original kaolinite	2.0	0.951	–	–
		0.3 CEC	34.3	0.991	0.84	4.08×10^3
		0.5 CEC	36.0	0.997	1.57	2.29×10^3
		0.7 CEC	37.6	0.995	1.90	1.98×10^3
		1.0 CEC	40.9	0.997	2.14	1.91×10^3
	CTMAB-bentonites	Original bentonite	8.4	0.894	–	–
		0.3 CEC	41.8	0.988	3.60	1.16×10^3
		0.5 CEC	79.0	0.994	6.97	1.13×10^3
		0.7 CEC	128.8	0.996	9.77	1.32×10^3
		1.0 CEC	205.6	0.999	15.50	1.33×10^3
DCB	CTMAB-kaolinites	Original kaolinite	1.2	0.678	–	–
		0.3 CEC	43.0	0.997	0.84	5.12×10^3
		0.5 CEC	50.6	0.998	1.57	3.22×10^3
		0.7 CEC	52.7	0.997	1.90	2.77×10^3
		1.0 CEC	54.2	0.996	2.14	2.53×10^3
	CTMAB-bentonites	Original bentonite	1.8	0.854	–	–
		0.3 CEC	64.6	0.988	3.60	1.79×10^3
		0.5 CEC	97.4	0.993	6.97	1.40×10^3
		0.7 CEC	153.3	0.983	9.77	1.57×10^3
		1.0 CEC	225.8	0.996	15.50	1.46×10^3
TCB	CTMAB-kaolinites	Original kaolinite	2.0	0.942	–	–
		0.3 CEC	53.0	0.987	0.84	6.31×10^3
		0.5 CEC	78.0	0.992	1.57	4.97×10^3
		0.7 CEC	92.5	0.988	1.90	4.87×10^3
		1.0 CEC	119.0	0.996	2.14	5.56×10^3
	CTMAB-bentonites	Original bentonite	2.6	0.964	–	–
		0.3 CEC	70.0	0.994	3.60	1.94×10^3
		0.5 CEC	105.9	0.990	6.97	1.52×10^3
		0.7 CEC	255.6	0.997	9.77	2.62×10^3
		1.0 CEC	377.6	0.996	15.50	2.44×10^3
TeCB	CTMAB-kaolinites	Original kaolinite	0.6	0.617	–	–
		0.3 CEC	57.0	0.993	0.84	6.79×10^3
		0.5 CEC	102.9	0.978	1.57	6.55×10^3
		0.7 CEC	113.7	0.991	1.90	5.98×10^3
		1.0 CEC	132.4	0.994	2.14	6.19×10^3
	CTMAB-bentonites	Original bentonite	9.6	0.898	–	–
		0.3 CEC	87.9	0.992	3.60	2.44×10^3
		0.5 CEC	276.1	0.991	6.97	3.96×10^3
		0.7 CEC	460.1	0.992	9.77	4.71×10^3
		1.0 CEC	1219.9	0.992	15.50	7.87×10^3

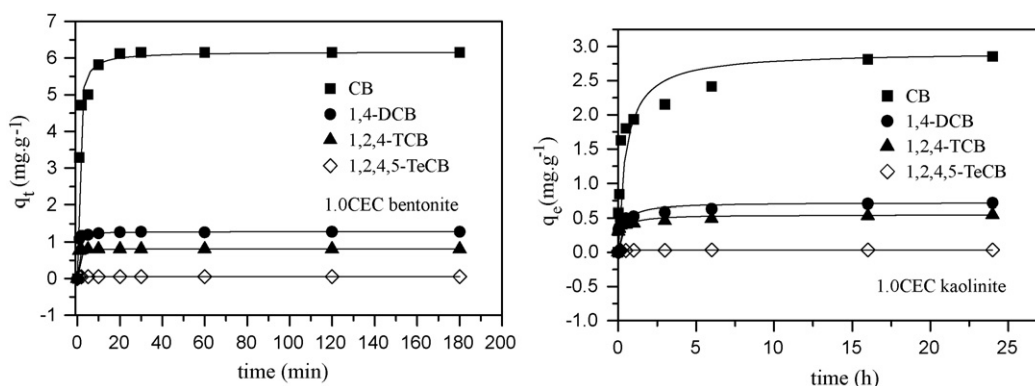


Fig. 3. Effect of contact time on the sorption of CBs onto CTMAB modified bentonite and kaolinite (the initial concentrations of CB, 1,4-DCB, 1,2,4-TCB and 1,2,4,5-TeCB were 100, 20, 10 and 0.6 mg L^{-1}).

order equations are analyzed. The pseudo-first-order model is given by Eq. (3) [20]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where k_1 is the pseudo-first-order rate constant (min^{-1}) and q_e is the pseudo-equilibrium sorption amount.

On the other hand, the pseudo-second-order model is expressed as Eq. (4) [21]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{1}{q_e} \right) t \quad (4)$$

where k_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{ min}^{-1}$).

The above-mentioned two models basically include all steps of sorption such as external film diffusion, sorption, and internal particle diffusion, so they are pseudo-models. The parameters

Table 3
Kinetics parameters for sorption of CBs on CTMAB modified bentonite and kaolinite.

Sorberent	Sorbate	Pseudo-first-order			Pseudo-second-order			Intra-particle diffusion	
		k_1	q_e	R^2	k_2	q_e	R^2	k_i	R^2
1.0 CEC bentonite	CB	0.041	0.224	0.531	0.282	6.173	0.999	0.155	0.459
	1,4-DCB	2.234	0.964	0.535	2.491	1.279	1.000	0.011	0.526
	1,2,4-TCB	0.147	0.025	0.884	22.53	0.808	0.992	0.0021	0.358
	1,2,4,5-TeCB	0.084	0.002	0.663	185.1	0.054	0.998	0.0002	0.348
1.0 CEC kaolinite	CB	0.156	1.429	0.954	0.676	2.925	0.986	0.2766	0.964
	1,4-DCB	0.231	0.330	0.927	4.416	0.721	0.998	0.0567	0.961
	1,2,4-TCB	0.159	0.201	0.899	7.129	0.548	0.999	0.0347	0.969
	1,2,4,5-TeCB	0.233	0.0095	0.962	227.1	0.034	0.999	0.0018	0.944

in these two models are determined from the linear plots of $\ln(q_e - q_t)$ versus t and t/q_t versus t , respectively. The results are shown in Table 3. It is found that the correlation coefficients for pseudo-first-order model are not high for CBs sorption onto both CTMAB-bentonites and CTMAB-kaolinites, moreover, the q_e calculated from the pseudo-first-order model is not consistent with the experiment data. However, good correlation coefficients are obtained by fitting the experimental data to Eq. (4), indicating that the sorption process for CBs is the pseudo-second-order. Fig. 3 also shows the typical curves in relation to the sets of data calculated from the constants of pseudo-second-order model in Table 3. The experimental points are shown together with the theoretically generated curves. The agreement between the sets of data reflects the extremely high correlation coefficients obtained and shown in Table 3. At the same time, the q_e calculated from the pseudo-second-order model for CBs sorption onto both CTMAB-bentonites and CTMAB-kaolinites are consistent with the results in Fig. 3. The sorption of CBs onto both CTMAB-bentonites and CTMAB-kaolinites could be a pseudo-second-order process rather than first-order.

Because the above two models cannot identify the sorption mechanism, the intra-particle diffusion model is tested in this work. It is originated from Fick's second law and is simply written as Eq. (5) [20]:

$$q_t = k_i t^{0.5} \quad (5)$$

where k_i is the rate constant of intra-particle diffusion ($\text{mg g}^{-1} \text{min}^{-0.5}$) and is determined from the linear plot of q_t versus $t^{0.5}$. In theory, such types of plots may present a multi-linearity, indicating that two or more steps occur [20,22]. The first portion (sharper) is the external surfaces sorption or instantaneous sorption stage (stage 1). The second portion is the gradual sorption stage (stage 2), where intra-particle diffusion is rate-controlled. The third portion is the final equilibrium stage (stage 3) where intra-particle diffusion starts to slow down due to extremely low solute concentrations in the solution. Results of this analysis on the CBs data are illustrated in Fig. 4 as plots of q_t versus $t^{0.5}$. The rate constant k_i is shown in Table 3. It is found that sorption of CBs onto CTMAB-kaolinite followed the intra-particle diffusion model better than that onto CTMAB-bentonite (the linear figure of CBs sorption onto CTMAB-bentonite is not shown). In fact, the intra-particle diffusion model is not suitable to illustrate CBs sorption process onto CTMAB-bentonite, which can be known from the correlation coefficients.

The plots of q_t versus $t^{0.5}$ (Fig. 4) are found to be linear with regression coefficients larger than 0.94. The linearity of the plots demonstrated that intra-particle diffusion played a significant role in the uptake of the CBs by CTMAB-kaolinite [23]. In Fig. 4, the intra-particle diffusion model shows that the external surface adsorption (stage 1) is less apparent for sorption of CBs onto CTMAB-kaolinite. Stage 1 completes within about 10 min and the stage of intra-particle diffusion control (stage 2) then attains. However, stage 3 (final equilibrium stage) is absent here over the whole range. As has

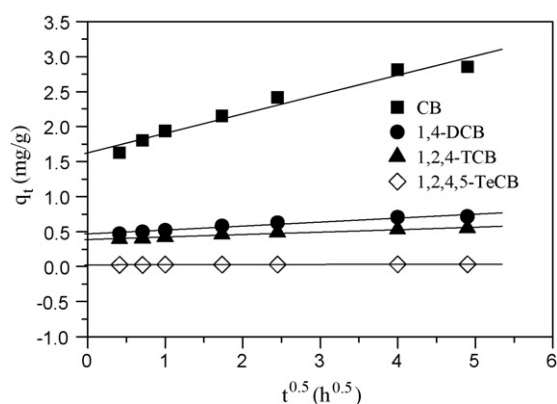


Fig. 4. Plots of intra-particle diffusion model for sorption of CBs onto 1.0 CEC kaolinite (the condition was the same as those indicated in Fig. 3).

been discussed above, the CBs slowly transport via intra-particle diffusion into the particles and finally retain in micropores.

The difference of intra-particle diffusion model characteristics between CBs sorption onto CTMAB-bentonite and CTMAB-kaolinite is because the tight and ordered combination of CTMAB-kaolinite have more apparent mass transfer blockage than CTMAB-bentonite to some extent [24].

3.3. Sorption thermodynamics

Experiments were carried out at three different temperatures to investigate CBs sorption onto 1.0 CEC CTMAB-bentonite and 1.0 CEC CTMAB-kaolinite. It is observed that the sorption of CBs decrease with increase of temperature (Fig. 5 or Table 4). The CBs sorption on both CTMAB-bentonite and CTMAB-kaolinite is definitely exothermic in nature requiring some amount of activation.

The thermodynamic parameters, such as standard free energy (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were calculated to evaluate the feasibility and exothermic nature of the sorption process. These parameters were obtained from the tests carried out at different temperatures using the following equations [25]:

$$\log K_d = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (6)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (7)$$

where K_d is the sorption coefficient. The value of ΔH^0 and ΔS^0 was determined from the slope and the intercept of the linear plot of $\log K_d$ versus $1/T$. These values were used to calculate ΔG^0 . These thermodynamic parameters are given in Table 4.

The ΔH^0 values of CBs sorption on CTMAB-bentonite and CTMAB-kaolinite are in the range of -4.57 to $-9.84 \text{ kJ mol}^{-1}$ and -7.36 to $-9.15 \text{ kJ mol}^{-1}$, respectively. The negative values conform to the exothermic nature of the sorption process. Similar exother-

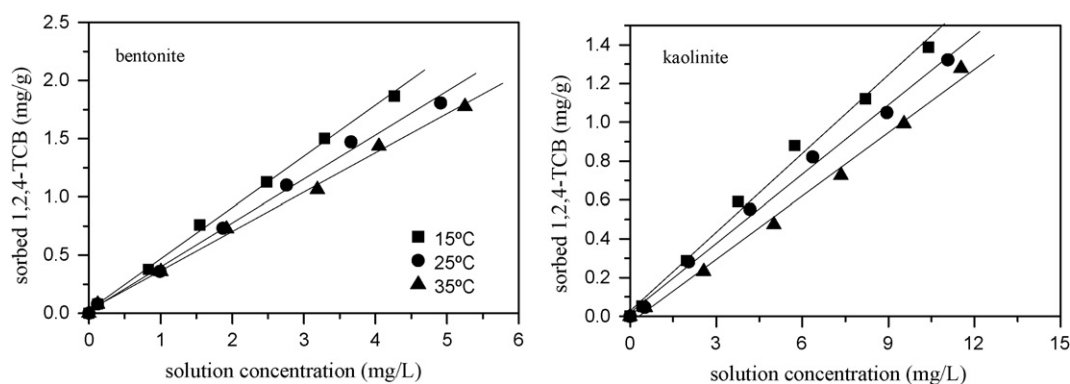


Fig. 5. Sorption of 1,2,4-TCB by 1.0 CEC CTMAB-bentonite and 1.0 CEC CTMAB-kaolinite.

Table 4

Thermodynamic parameters for the sorption of CBs on CTMAB-bentonite (C-B) and CTMAB-kaolinite (C-K).

Parameters	CB		DCB		TCB		TeCB	
	C-K	C-B	C-K	C-B	C-K	C-B	C-K	C-B
$-\Delta H^0$ (kJ mol ⁻¹)	9.15	9.58	7.44	8.24	8.00	9.84	7.36	4.57
ΔS^0 (J mol ⁻¹ K ⁻¹)	6.34	12.34	8.28	17.30	12.99	16.39	15.92	43.72
$-\Delta G^0$ (kJ mol ⁻¹)								
$T=288$ K	10.98	13.13	9.83	13.22	11.74	14.56	11.95	17.16
$T=298$ K	11.04	13.25	9.91	13.39	11.87	14.72	12.11	17.60
$T=308$ K	11.10	13.38	9.99	13.57	12.00	14.89	12.27	18.03

mic sorption of CBs was observed earlier on soil, sediment and phenyl coated silica [26,27].

The magnitude of sorption enthalpy change may give an idea about the type of sorption. In this test, the small values of ΔH^0 are compatible with the following concept: for hydrophobic organic compounds without any strong polar groups, the main driving force behind the sorption process is so called “hydrophobic sorption”, a term used for the combination of London–Van der Waals interactions between solute and sorbent [28]. The other sorption forces only play a minor role for CBs. Hamaker and Thompson [29] stated that the effect of temperature on the sorption equilibrium is a direct indication of the strength of the sorption. For weaker bonds, less influence of temperature is expected because of the lower equilibrium sorption enthalpy change.

The sorption process results in an increase in entropy of 12.3–43.7 J mol⁻¹ K⁻¹ and 6.3–15.9 J mol⁻¹ K⁻¹, respectively for CTMAB-coated bentonite and kaolinite. Positive ΔS^0 value corresponds to an increase in degree of freedom of the adsorbed species. Usually, sorption of gases on solids is accompanied by a decrease in entropy, because the molecules from the disordered gaseous state form an ordered arrangement on the surface of the solids. In the case of sorption from solutions, it is likely that the CBs molecules on CTMAB-clays surface are more chaotically arranged compared to the situation in aqueous solution. The large CBs molecules might be responsible for this. The positive values of ΔS^0 conform to a high preference of CBs molecules for the CTMAB-clays surface.

The negative ΔG^0 values confirm the feasibility of the sorption process and the spontaneous nature of sorption. The rise in ΔG^0 with rise in temperature shows that the reaction is more favorable at high temperatures. The extent of CBs sorption decreases because desorption increases with temperature. The parameters, ΔH^0 , ΔS^0 , and ΔG^0 , for CBs–organoclays interactions change in a way that makes the sorption thermodynamically feasible with a high degree of affinity of CBs molecules for the CTMAB-bentonite or CTMAB-kaolinite surfaces.

The similar values of ΔH^0 , ΔS^0 and ΔG^0 for CTMAB-bentonite and CTMAB-kaolinite indicate that the mechanism for CBs sorption

on them are all about the same, which can be seen from the sorption isotherms above-mentioned.

4. Conclusions

The experimental data, which produced perfect fit with linear isotherm, show that the mechanism of CBs sorption onto CTMAB modified bentonite and kaolinite is through a distribution process. The distribution coefficient K_d is primarily affected by the amount of sorbed surfactant. The Sorption of CBs is dependent on arrangement of sorbed surfactant cations, which are affected by the underlying mineral type and the mass fraction of carbon.

The sorption of CBs onto both CTMAB-bentonites and CTMAB-kaolinites follows pseudo-second-order kinetics. The sorption of CBs onto CTMAB-kaolinite also follows the intra-particle diffusion model, while, the intra-particle diffusion model is not suitable to illustrate CBs sorption process onto CTMAB-bentonite.

The sorption of CBs on both CTMAB-bentonites and CTMAB-kaolinites is exothermic in nature and accompanied by an increase in entropy and a decrease in Gibbs energy in the temperature range of 15–35 °C. The similar values of ΔH^0 , ΔS^0 and ΔG^0 for CTMAB-bentonite and CTMAB-kaolinite indicate that the mechanism for CBs sorption on them is the same.

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