

Removal of catechol from aqueous solutions by adsorption onto organophilic-bentonite

K. Shakir^{a,*}, H.F. Ghoneimy^a, A.F. Elkafrawy^b, Sh.G. Beheir^a, M. Refaat^a

^a Nuclear Chemistry Department, Hot Laboratories Center, Atomic Energy Authority Post 13759, Cairo, Egypt

^b Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt

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Abstract

Organophilic-bentonite, produced by exchange of cetyltrimethylammonium cation for metal cations on the bentonite, was exploited as adsorbent for removal of catechol from aqueous solutions using batch technique. The dependence of removal on various physico-chemical parameters, such as contact time (1–250 min), concentration (0.8–15.3 mmol L⁻¹), temperature (30, 40, 50 ± 1 °C) and pH (5–12) of the adsorptive solution were investigated. Obtained results show that catechol could be removed efficiently (~100%) at pH values ≥ 9.9. The uptake process follows first-order rate kinetics and the equilibrium data fit well into the Langmuir and Freundlich adsorption isotherms over a wide range of concentration (1–10 mmol L⁻¹). The magnitude of change of free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Catechol, pyrocatechol or *o*-hydroxyphenol, is used as a topical antiseptic, and in photography, fur dyeing, leather tanning, antifungal preservation of seed potato pieces, and in polymerization inhibitors as well as a chemical intermediate, and an antioxidant in many industries [1,2]. It is also used in chemical laboratories for the detection and determination of many ions. Catechol, therefore, frequently contaminates wastewaters generated by several industries including rubbers, chemical, dye, photographic, pharmaceutical, cosmetics, and oil industry [3]. The effluents from synthetic coal fuel conversion processes may contain catechol and resorcinol concentrations ranging from a few mg L⁻¹ to 1000 mg L⁻¹ [4]. Catechol, like other phenols, is of particular interest from a sanitary point of view due to its toxicity and deleterious effect on the quality of water supplies. The compound is readily absorbed from the gastrointestinal tract, causes hemolysis, degenerates the renal tubes, diminishes liver function, and accumulates in the bone marrow [5]. Its metabolites may initiate many cancers and neurodegenerative

diseases [6]. Catechol is even more toxic than phenol since it provokes changes in the function of erythrocytes at doses as low as 50 µg L⁻¹ compared to 250 µg L⁻¹ of phenol [7].

The United States Environmental Protection Agency (EPA) [8] has ranked phenols the 11th in list of 126 toxic chemicals that have been designated as priority pollutants and stringent restrictions have been imposed by local authorities on levels of phenol contaminants in water and wastewater. According to the Egyptian regulations the concentration of phenols in the industrial effluents should not exceed 0.05 and 1 mg L⁻¹ for safe discharge in sewage [9] and in marine environment [10], respectively. Therefore, removal of catechol from water or wastewater is of great importance. A number of technologies have been used for the removal of catechol from water and aqueous solutions. These include destructive processes such as destructive oxidation, adsorptive micellar flocculation, ultra-filtration, biological methods and adsorption on organic and inorganic compounds. Of these technologies adsorption on activated carbon still remains the most common process used for removal of catechol and other phenolecyl pollutants, especially for water with moderate and low pollutant concentration [11]. However, activated carbon can be advantageously used only in particular cases because of its high cost [12]. Therefore, attention has been directed to less expensive materials.

* Corresponding author.

E-mail address: kshakir@lycos.com (K. Shakir).

Over the last few decades organo-clays have gained much importance for the removal of organic pollutants from aqueous solutions. Among the various types of clays, montmorillonite which is the main constituent of the low cost and naturally abundant mineral bentonite possesses several of the properties that make it very appropriate for organo-clay preparation. Montmorillonite has a 2:1 type layer consisting of one octahedral sheet of alumina inserted in between two silica tetrahedral sheets. In the tetrahedral sheets, Al^{3+} can substitute for Si^{4+} and in the octahedral sheets Mg^{2+} or Zn^{2+} can replace Al^{3+} . These isomorphous substitutions in the clay lattice result into a net negative charge on the clay surface [13]. Interlayer cations, usually sodium or calcium, balance the total electrostatic charge. Under these conditions of diminished interlayer attraction, water can interleave between layers rendering each triple layer surface equivalent to an exterior one, and the balancing interlayer ions can exchange [14]. In aqueous solutions, large quaternary ammonium organic cations can readily replace the native exchangeable inorganic cations in the interlamellar space of the clay mineral by ion exchange and are said to be “intercalated” by the mineral [15]. The sorption properties of the resulting organo-clay surfaces may be significantly altered by this exchange reaction and the clay may become organophilic and its capability to remove organic pollutants from aqueous solutions may be greatly increased [16–18]. Investigations [16,17] indicate that the magnitude and mechanism of sorption are functions of the cation-exchange capacity of the clay, the molecular structure of the exchanged organic cation, the extent of cation exchange, and the molecular structure of the solute. Sorption may take place either by partition or by adsorption depending mainly on the characteristics of the exchanged organic cation and the molecular structure of the solute.

Organo-clays synthesized with various quaternary ammonium cations have been intensively investigated [16–22] and applied for removal of various organic contaminants from water and wastewater but no studies have, so far, appeared in the literature on the adsorption behavior of catechol. This paper presents the experimental results of equilibrium and kinetics of catechol adsorption, from aqueous solutions of varying pH values, on cetyltrimethylammonium bromide-modified bentonite (CTAB-B).

2. Experimental

2.1. Materials

Bentonite used was primarily Na^+ -montmorillonite. It is exploited from Kasr El Sagha, Fayoum, Egypt and is commercially available. The cation exchange capacity (CEC) of bentonite was determined by the methylene blue-acid titration method [23] and has been found to be 695 mmol kg^{-1} of bentonite.

Cetyltrimethylammonium bromide (CTAB) used for CTAB-bentonite (CTAB-B) preparation was of analytical grade and was purchased from Aldrich Chemical Co.

A stock solution of 0.01 M catechol was prepared by dissolving appropriate weight of Analar $\text{C}_6\text{H}_6\text{O}_2$ provided by

Merck. Catechol solution was preserved in dark reagent bottles.

Hydrochloric acid and sodium hydroxide solutions, prepared from analytical grade chemicals, were used for pH adjustment. Double distilled water was used in all experiments.

2.2. Preparation of CTAB-bentonite (CTAB-B)

Natural bentonite (N-B) was gently crushed, ground in a rod mill (closed circuit) and then sieved. The $53 \mu\text{m}$ fraction was oven-heated at 85°C for 3 h and finally dried for 1 h at 105°C .

For CTAB-B preparation, 25 g sample of the dried bentonite was added to 250 mL of water containing 5 g of CTAB (corresponding to $\sim 79\%$ of the CEC). The suspension was then shaken, at 65°C , for 4 h. The treated clay was left over-night to settle and the supernatant solution was separated by decantation. The treated clay was then washed by shaking with 250 mL of water for 1 h, left to settle and then separated. The washing process was repeated several times until the washings were free from bromide ions as indicated by AgNO_3 . The organobentonite was at last separated from water by vacuum filtration, dried at 80°C , activated for 1 h at 105°C , and gently ground with a mortar and pestle to break up aggregate particles.

The amount of CTAB sorbed to bentonite was determined by two methods: (1) from the results of the organic carbon content, determined by elemental analysis performed in the Analytical Services Unit at the National Research Center, using Vario Elementr CHN analyzer, and (2) as the difference between the initial and final amount of CTAB in solution, determined spectrophotometrically by the bromothymol blue method [24]. The amount of organic carbon in raw bentonite was nil and that of CTAB sorbed was calculated as 77.9% and 78.7% of the CEC, as found spectrophotometrically and by elemental analysis, respectively.

2.3. Sorption studies

For sorption studies, 0.25 g samples of CTAB-B were taken in 50 mL bottles containing varying amounts of catechol solution of the required pH and the volume was adjusted to 25 mL with bidistilled water. The bottles were then well closed and shaken for 45 min, except where the effect of time was investigated, in an electric temperature-controlled shaker. Unless otherwise specified, the initial catechol concentration was kept constant at $8 \times 10^{-4} \text{ M}$ ($\sim 88 \text{ mg L}^{-1}$), the temperature was $30 \pm 1^\circ\text{C}$, the pH was adjusted to 11.3 ± 0.1 . The suspensions were then centrifuged, 5 mL of the supernatant solution was withdrawn and the catechol amount remaining in the supernatant solution was determined spectrophotometrically. Though a number of methods have been proposed in the literature for spectrophotometric determination of phenols, none of them seemed sufficiently selective to be useful for catechol determination in the concerned solutions. Therefore, a spectrophotometric study for its determination was performed which led to the development of a simple and sufficiently selective and reliable method for its determination [25]. The method is based on that a catechol solution develops a violet color at high pH and consists in measuring the absorption of the solution of catechol at 450 nm and pH

10.5–12 in presence of CTAB (0.005 M), against a reference blank of similar pH value and CTAB concentration. The absorption being constant in the course of 6 h, after which it remains unchanged for more than 24 h. Experiments have shown that ions which might dissolve from the clay in the pH range tested do not affect the color intensity. Beer's law is obeyed over the range 0.0–6.6 μg catechol mL^{-1} .

The amount of catechol adsorbed was estimated as the difference between its initial amount and that left after equilibration. The reported results are the mean values of at least two experiments.

3. Results and discussion

3.1. Effect of pH

The effect of pH on adsorption of catechol on N-B and CTAB-B was studied by varying the pH of the solution from about 5 to 12. The results are depicted in Fig. 1 which shows that adsorption of catechol on N-B is almost negligible (Fig. 1, curve a). This result is quite expected since aqueous solutions of catechol are weakly acidic and untreated montmorillonite is hydrophilic and negatively charged, hence catechol cannot be adsorbed on N-B due to charge repulsion. A similar observation has been reported [21] for the uptake of phenol onto montmorillonite. Fig. 1 also shows the dramatic effect of CTAB treatment on the adsorption of catechol by bentonite. However, the adsorption strongly depends on the pH of the solution. The percentage adsorption remains low, $\leq 11\%$, up to about pH 7.5 where it increases sharply with pH to attain about 100% at $\text{pH} \geq 9.9$. These results can be best interpreted in terms of the sorptive properties of CTAB and the dissociation of catechol. Adsorption of the large cationic surfactant molecule, CTAB, greatly modifies the nature of clay surface which may exhibit both hydrophilic and hydrophobic as well as electrostatic properties and van der Waals interaction between the $-\text{R}$ group of the surfactant and adsorbate [18,20]. Therefore, catechol may be adsorbed and

retained onto CTAB-B by various mechanisms, mainly depending on the solution conditions. In aqueous solutions, catechol can dissociate into the negatively charged catechol oxide ion. Being a weak acid, the dissociation strongly depends on the pH of solution and increases with pH elevation. Variation of the extent of dissociation with pH-change can be theoretically calculated. Thus, if it is assumed that the dissociation products are completely removed from the solution (ca. by adsorption) as soon as they are formed, an adsorption-pH curve, that is a dissociation-pH curve, can be theoretically calculated from the dissociation constant of the adsorbate ($\text{p}K_a$ of catechol = 9.48 [26]) and the relation:

$$\text{Adsorption \%} (\equiv \text{dissociation \%}) = \frac{1}{1 + 10^{(\text{p}K_a - \text{pH})}} \times 100$$

To compare with the experimental adsorption curve, the calculated curve (curve c) is included in Fig. 1 and shows that at pH 7.5 adsorption starts to increase sharply with pH elevation in coincident with the experimental adsorption curve (Fig. 1, curve b). At pH below 7.5 dissociation is insignificant ($< 1.0\%$), that is catechol exists mainly as the non-charged molecule. However, the extent of adsorption obtained experimentally at a given pH is seen to be higher than theoretically predicted. The observed increase in adsorption at pH values > 7.5 is a consequence of the dynamic nature of the simultaneous equilibria between dissociated and undissociated species. Thus, removal of the dissociation products from the solution (ca. by adsorption) accelerates dissociation as a result of the simultaneous equilibria which in turn results in increase in adsorption. From the foregoing it is concluded that the removals obtained at pH values higher than 7.5 are primarily due to favorable electrostatic interaction between the negatively charged catechol oxide ion and positively charged surfaces of the modified-bentonite particles. On the other hand, the relatively low removals observed at pH values < 7.5 can be mainly attributed to van der Waals interaction between uncharged catechol molecules and $-\text{R}$ groups of the quaternary ammonium ion. This observation is consistent with the findings reported by others [20] for adsorption of phenolic compounds onto hexadecyltrimethylammonium-treated montmorillonite.

3.2. Effect of contact time and initial catechol concentration

The uptake of catechol, by CTAB-B, at different values of pH ca. 5.4, 8.3 and 11.3 was studied as a function of shaking time by varying the time from 1 to 250 min as presented in Fig. 2. The results show that the rate of adsorption of catechol strongly depends on the pH of the solution and is initially quite rapid with most of the compound being adsorbed within the first few minutes. The rate of adsorption then slows down with the elapse of time until an apparent equilibrium is reached. At the highest and lowest pH values tested (5.4 and 11.3), equilibrium is attained in about 15 min, but at pH 8.3 about 2 h are required to reach equilibrium. Therefore, in the subsequent experiments, the shaking time was set at 45 min for solutions of pH 5.4 and 11.3 and at 150 min for solutions of pH 8.3, to

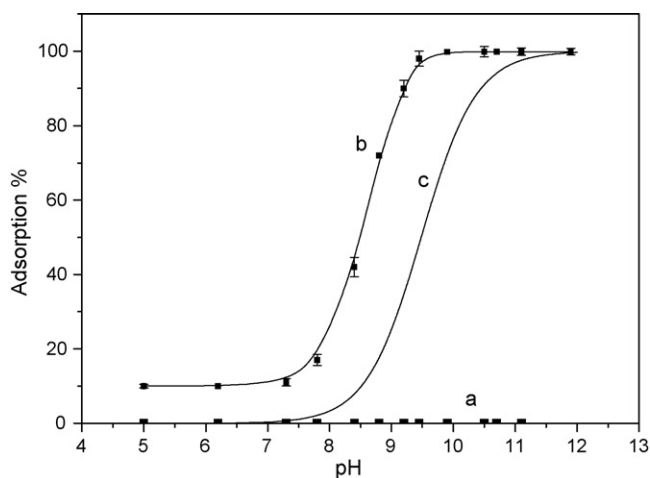


Fig. 1. Experimental and calculated curves for adsorption of catechol at 8×10^{-4} M vs. pH using N-B and CTAB-B. (a) N-B, (b) CTAB-B, experimental, and (c) calculated. Error bars are the standard deviation estimate for the average of three experiments.

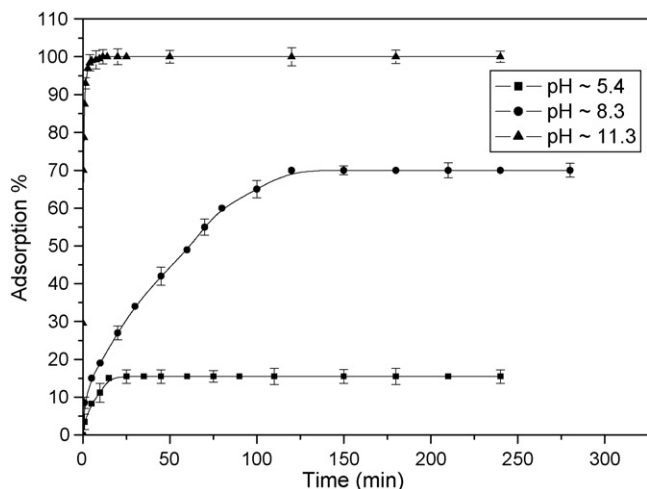


Fig. 2. Time dependence of adsorption on CTAB-B at various values of pH. Catechol 8×10^{-4} M. Error bars are the standard deviation estimate for the average of three experiments.

ensure equilibrium. The results (Fig. 2) also show the strong influence of pH on the distribution of catechol between the adsorbate and solution. The adsorption of catechol onto CTAB-B was further examined as a function of time of contact at various initial catechol concentrations ca. 8×10^{-4} M, 2×10^{-3} M and 3×10^{-3} M. As shown from Fig. 3, the amount of catechol adsorbed at equilibrium per gram of adsorbate increases from 0.07 to 0.244 mmol g^{-1} with increase in the initial concentration over the range tested, due to the increase in the mass driving force which enforces more catechol ionic species to pass from the bulk solution to the clay surface at a given time. On the contrary, the percentage adsorption increases from 81.5% to $\sim 100\%$ as the initial adsorbate concentration is reduced from 3×10^{-3} M to 8×10^{-4} M. This observed increase in the percentage adsorption is due to the availability of larger sorbent surface sites for relatively smaller amount of catechol at lower concentrations.

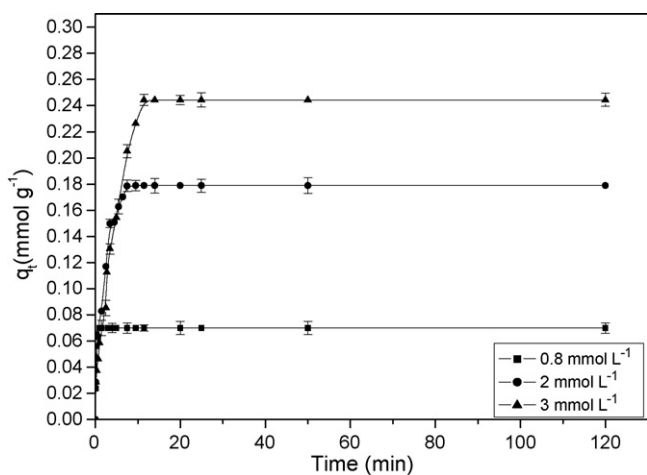


Fig. 3. mmol adsorption g^{-1} adsorbent at pH 11.2 and various initial catechol concentration vs. time. Error bars are the standard deviation estimate for the average of three experiments.

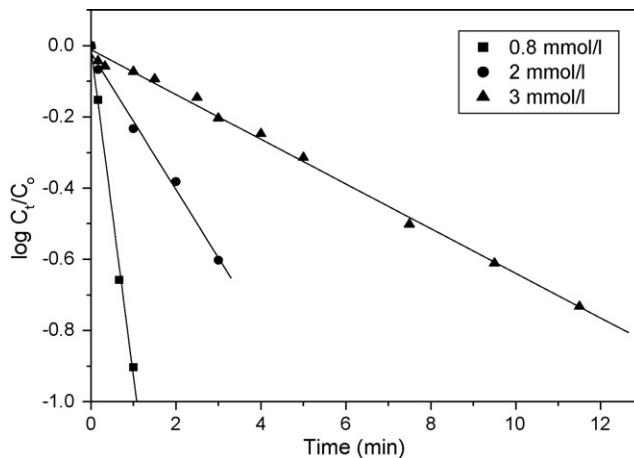


Fig. 4. Plots of log adsorption decay during the initial stage at pH 11.2 and various initial catechol concentration vs. time.

3.3. Kinetic studies

To understand and predict how time affects mobility and retention of adsorbates, it is important to study the kinetic of the adsorption process. For this purpose, different kinetic models as first-order [12,22], pseudo-first-order [27,28] and pseudo-second-order [27] rate equations have been applied by different authors to characterize adsorption processes. In the present case, data obtained from Fig. 3 were used to construct plots of the logarithmic decay of catechol, i.e. C_t/C_0 versus t (where C_t and C_0 are the catechol concentration at times t and zero, respectively) during the initial stage of adsorption. As shown from Fig. 4, the obtained plots are linear and pass through the origin, thus indicating an apparent first-order adsorption of catechol by CTAB-B. This finding was further confirmed by applying the pseudo Lagregran's equation [12,22]:

$$\ln(q_e - q_t) = \ln q_e - K_a t \quad (1)$$

where q_e and q_t are the amounts of catechol adsorbed at equilibrium and at time t , respectively and K_a is the pseudo-first-order-rate constant. As shown from Fig. 5, plots of $\ln(q_e - q_t)$ versus t , obtained at the three different initial catechol concentrations examined, are linear with correlation coefficients ≥ 0.986 , indicating that the Lagregran's equation is applicable to the present system and that the adsorption process is pseudo-first-order one. Values of K_a calculated from the plots as well as the half-lives ($t_{1/2} = \log_e 2/K_a$ [29]) for catechol adsorption onto CTAB-B and correlation coefficients are depicted in Table 1. The values of $t_{1/2}$ at 0.8, 2, and 3 mmol catechol L^{-1} are 0.945, 1.561, and 3.742 min, respectively indicating that the

Table 1
Lagregran's rate constants, half-lives, and correlation coefficients for catechol adsorption at various initial concentrations (C_0)

C_0 (mmol L^{-1})	K_a (min^{-1})	$t_{1/2}$ (min)	r^2
0.8	0.7359 ± 0.052	0.945 ± 0.0456	0.988
2	0.4457 ± 0.034	1.561 ± 0.0816	0.986
3	0.1858 ± 0.013	3.742 ± 0.1789	0.986

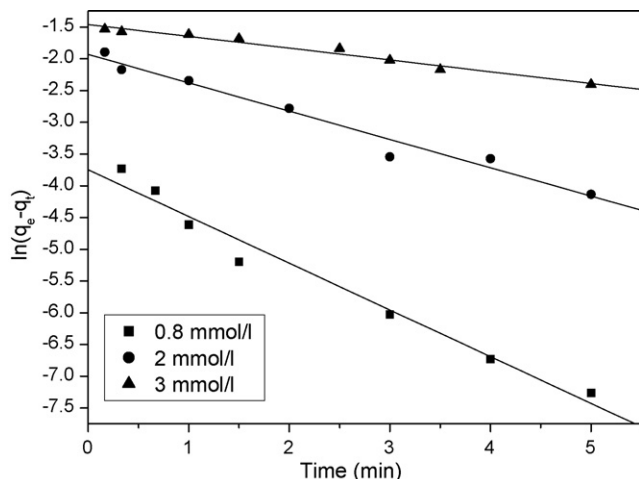


Fig. 5. Lagregran plots for catechol adsorption at pH 11.2 and various initial concentrations.

rate of adsorption increases with decrease in the initial catechol concentration.

To identify the diffusion mechanism that controls the present adsorption system, the kinetic data were further analyzed by the widely applied intraparticle diffusion model [27,30]. The linear form of this model can be represented by the equation [31]:

$$q_t = k_p t^{1/2} + C \quad (2)$$

where k_p is the intraparticle diffusion constant ($\text{mmol g}^{-1} \text{min}^{-1/2}$), and the value of the intercept C is indicative of the boundary layer. According to this model, plots of q_t versus $t^{1/2}$ should be linear and pass through the origin if intraparticle diffusion is the rate controlling step [31]. On the other hand, if the plots are linear but do not pass through the origin the rate of adsorption may be controlled by intraparticle diffusion together with other kinetic models. As shown from Fig. 6, plots of q_t versus $t^{1/2}$ at different pH values are all linear with correlation factors >0.97 and pass through the origin thus indicating that intraparticle diffusion is the rate controlling step in the present system. From the plots in Fig. 6, values of k_p

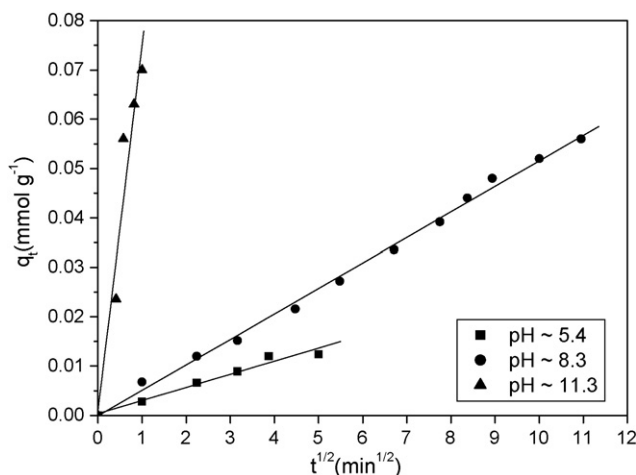


Fig. 6. Plots of adsorption at 0.8 mmol L^{-1} and various pH values vs. square root of contact time.

Table 2

Intraparticle diffusion constants (k_p) and correlation coefficients for catechol adsorption at different pH values

pH	k_p ($\text{mmol g}^{-1} \text{min}^{-1/2}$)	r^2
5.4	0.0027 ± 0.00023	0.985
8.3	0.0052 ± 0.00009	0.998
11.3	0.0742 ± 0.01159	0.97

were calculated and are given along with the correlation factors in Table 2.

3.4. Equilibrium studies

3.4.1. Adsorption isotherms

Adsorption isotherms were determined at different pH values, ca. 5.4, 8.3 and 11.3 as a function of temperature, by varying the initial catechol concentration and keeping the CTAB-B mass constant. The isotherms obtained at pH 11.3 and three different temperatures ca. $30, 40, 50 \pm 1^\circ \text{C}$ are shown in Fig. 7 and those achieved at $30 \pm 1^\circ \text{C}$ and pH 5.4 and 8.3 are presented in Fig. 8. From the curves plotted in Fig. 7, the saturation capacity at pH 11.3 was determined for the three temperatures tested and are given in Table 3. As shown from this table, the extent of adsorption decreases with rise in temperature indicating the process is exothermic in nature.

Comparison of Figs. 7 and 8 shows that the adsorption isotherm profiles obtained at the higher and lower pH values tested, pH 11.3 (Fig. 7) and pH 5.4 (Fig. 8, curve a) are apparently alike but differ considerably from the isotherm at pH 8.3 (Fig. 8, curve b). As shown from the figures, the isotherms at pH 5.4 and 11.3 are of the L-shape (Langmuir type) which is characterized by a decreasing slope as the concentration of the adsorbate is increased due to progressive decrease in the availability of binding sites [32]. The steep rise exhibited by both isotherms (Figs. 7 and 8, curve a) at low concentrations of catechol indicates a high affinity of CTAB-B for catechol, whereas the almost leveling off of the isotherms in the region of saturation suggests

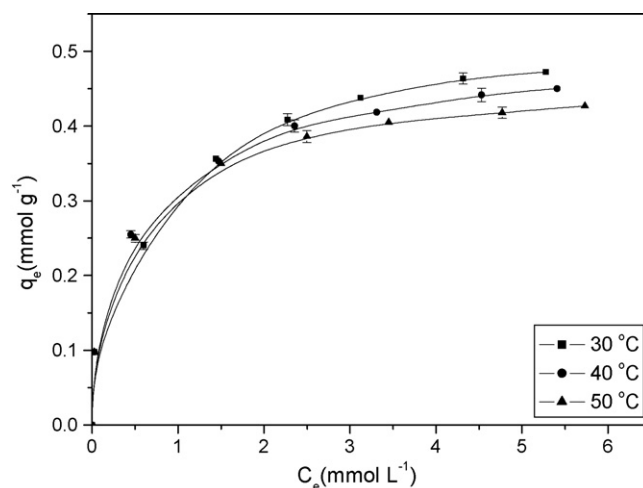


Fig. 7. Adsorption isotherms at pH ~ 11.3 and various temperatures. Error bars are the standard deviation estimate for the average of three experiments.

Table 3
Saturation capacities, Langmuir and Freundlich parameters and correlation coefficients (r^2) for catechol adsorption at pH ~ 11.3 and 30, 40, 50 ± 0.1 °C

Temperature (°C)	Saturation capacity (mmol g ⁻¹)	Langmuir coefficients			R_L	Freundlich coefficients		
		Q (mmol g ⁻¹)	K_L (L g ⁻¹)	r^2		$1/n$	K_f	r^2
30	0.472	0.507 ± 0.015	2.33 ± 0.51	0.995	0.313	0.305 ± 0.012	0.301 ± 0.004	0.996
40	0.454	0.476 ± 0.011	2.81 ± 0.65	0.997	0.264	0.288 ± 0.013	0.299 ± 0.0046	0.995
50	0.427	0.443 ± 0.007	3.13 ± 0.6	0.998	0.227	0.277 ± 0.015	0.287 ± 0.0052	0.993

that the over-all capacity can be taken advantage of in a wide range of equilibrium concentration of the adsorbate in the aqueous phase. On the other hand, the adsorption isotherm obtained at pH 8.3 seems to consist of two regions. The increase in adsorbed amount at the second region is more sharp and the slope increases more steeply with increasing solution concentration. Differences in the adsorption isotherm patterns observed at the different pH values tested can be interpreted in terms of adsorption behavior of the organo-clay and the ionization state of the adsorbate, catechol. Generally, there are two types of interaction between organic pollutants and clays modified with long carbon-chain alkyl ammonium cations, such as CTAB; these are partition and adsorption [16]. The former type indicates a mechanism in which the solute is solubilized into the organophilic bulk of the organo-clay and is usually described by a partitioning coefficient and characterized by a linear isotherm, non-competitive sorption, and relatively low solute uptake [16]. The latter type of uptake, adsorption, involves site specific adsorption and it usually obeys the Langmuir or Freundlich equation, exhibits high solute uptake and competitive sorption [16,33]. As shown from the results (Figs. 7 and 8) the isotherms are non-linear and the organo-clay has a high affinity to catechol as indicated by the L-type profile and the high removal, >80% even for the most concentrated solution tested (Fig. 3). These results indicate that catechol is primarily uptaken by adsorption. Partition, if existing, plays a minor or negligible role, presumably due to the large difference between the polarity of catechol (which is polar) and the non-polar organic medium of the organo-clay. Similar findings have

been reported in the literature for uptake of phenol and phenolic derivatives onto CTAB-modified bentonite [16,33]. Though the uptake of catechol at the lower and higher pH values tested is mainly due to adsorption, the adsorption mechanism expectedly differs due to differences in the type of catechol species that might exist in solution at the two different pHs. At pH 11.3, where catechol exists mainly in the anionic form, adsorption is most likely due to electrostatic attraction. According to the literature [34] when a long carbon-chain cationic surfactant, such as CTAB, is added to a clay it is initially adsorbed by cation-exchange in the interlayer causing extensive clay aggregation. As the loading is increased, the surfactant adsorbs to the external surfaces of aggregates via both cation-exchange and hydrophobic bonding. The latter, results in a building of positive charge on the clay surfaces exposed to the bulk solution [34,35–37] causing organo-clay disaggregation [34]. Considering that these effects of increased loading can occur even at surfactant concentration well below the CEC of the clay [34,36], it is very possible that under our experimental conditions clay surfaces develop positive charges. Electrostatic attraction of these positive charges with anionic catechol species is believed to be the cause of catechol adsorption at the higher pH value, pH 11.3.

At pH 5.4, catechol dissociation is minimum, or even negligible (Fig. 1); hence adsorption at that pH should be due to uptake of neutral molecule. Adsorption of neutral molecules of phenol and phenolic derivatives onto organo-clays was also observed [20] and has been attributed to van der Waals interaction of the solute with the tail group of the quaternary amine. At the intermediate pH value tested, pH 8.3, catechol exists in solution in both the neutral and anionic forms. Hence, it seems judicious to assume that at this pH catechol is adsorbed via both electrostatic and van der Waals interaction. This is believed to be the cause of the unusual profile of the isotherm (Fig. 8, curve b) and the different kinetics (Fig. 2) observed at pH 8.3 as compared with those achieved at the lower and higher pH values examined.

3.4.2. Adsorption models

The adsorption isotherms obtained at pH 11.3 were subjected to analysis in terms of the well known Langmuir and Freundlich adsorption models.

The Langmuir equation was originally derived assuming chemisorption and is theoretically derived from simple mass-action kinetics, yet it also has been widely applied to physical adsorption data [38]. The following well known linearized form of the Langmuir equation has been used to analyze the obtained

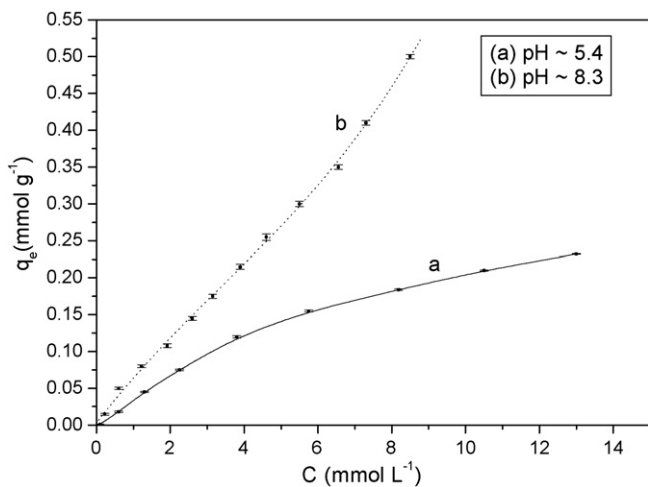


Fig. 8. Adsorption isotherms at pH ~ 5.4 (curve a) and 8.3 (curve b) at 30 ± 1 °C. Error bars are the standard deviation estimate for the average of three experiments.

adsorption results:

$$\frac{C_e}{q_e} = \frac{1}{QK_L} + \frac{C_e}{Q} \quad (3)$$

where C_e is the equilibrium concentration of catechol in solution (mmol L^{-1}); q_e the amount of catechol adsorbed per gram of CTAB-B (mmol g^{-1}); Q the adsorption maximum or what is generally termed the monolayer capacity and has the units of q_e (mmol g^{-1}); K_L is a constant related to the intensity of adsorption (L g^{-1} of adsorbent).

The plots of C_e/q_e versus C_e obtained at the three different temperatures tested (not shown for abbreviation) were found to be straight lines indicating conformity of the adsorption data with the Langmuir equation over the entire initial catechol concentration studied ($1\text{--}10\text{ mmol L}^{-1}$). From the slopes and intercepts of the straight lines the values of Q and K_L were estimated and are given in Table 3. The correlation factors are also depicted in the table and show that the linear fits of C_e/q_e versus C_e are fairly good.

The essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, R_L , which describes the type of isotherm and is defined by:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where K_L is the Langmuir constant and C_0 is the initial concentration of the adsorbate. The values of R_L calculated are between 0.0 and 1.0 (Table 3), indicating favorable adsorption of catechol on CTAB-B at all the temperatures examined.

The Freundlich isotherm is empirical and has been derived by assuming a heterogeneous surface with a uniform distribution of the heat of adsorption over the surface. The linear expression of this isotherm can be written:

$$\log q_e = \log K_f + \frac{1}{n}(\log C_e) \quad (5)$$

where C_e and q_e have the same definitions mentioned before, and K_f and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The parameter $1/n$ is considered to be between 0.0 and 1.0 and it is a measure of the heterogeneity of adsorption sites on the surface of the adsorbent [39].

Plots of $\log q_e$ versus $\log C_e$ (Eq. (5)) (not shown for abbreviation) were found to be straight lines indicating the validity of the Freundlich expression over the entire range of catechol concentration studied. From the slopes and intercepts of the straight lines, the values of K_f and $1/n$ have been determined by a least square fit program and are given along with the correlation factors (r^2) in Table 3. The relatively low values of $1/n$

(0.305–0.272) indicate a heterogeneous surface with an exponential distribution of the adsorption sites; that is all surface sites are not identical [40]. Table 3 also indicates that the parameters Q and K_f which are related to the sorption capacity decrease with an increase in the temperature. This is consistent with the experimental observations (Fig. 7), and supports the conclusion that the present sorption process is an exothermic one.

3.5. Thermodynamic parameters

The change in enthalpy, ΔH° , and entropy, ΔS° , associated with the adsorption of catechol on CTAB-B were determined by the equation:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

and the change in the standard free energy, ΔG° , was calculated using the equations:

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

and

$$\Delta G^\circ = -RT \ln K_d \quad (8)$$

where R ($\text{J mol}^{-1} \text{K}^{-1}$) is the gas constant, T (K) the absolute temperature and K_d is the distribution ratio:

$$K_d = \frac{\text{initial concentration} - \text{final concentration}}{\text{final concentration}} \times \frac{\text{volume of solution}}{\text{weight of adsorbate}}$$

As shown from Fig. 9, a plot of $\ln K_d$ versus $1/T$ yields a straight line from which ΔH° and ΔS° were estimated from the slope and intercept, respectively. The ΔG° values estimated from Eqs. (7) and (8) are in good agreement with each other and are given together with the values of ΔH° and ΔS° in Table 4. Generally, the magnitude of the change of free energy, ΔG° , can give information whether adsorption takes place by a physical or a chemical process. According to the literature [41], if ΔG° ranges between 0 and -20 kJ mol^{-1} , the adsorption process is of a physical nature, but if it ranges between -80 and -400 kJ mol^{-1} , the adsorption process is a chemical one. Hence, the numerical negative value of ΔG° (Table 4) obtained under the experimental conditions, indicates that adsorption of catechol by CTAB-B is a spontaneous physisorption process and that the system does not gain energy from the surroundings. The shift of the magnitude of the standard free energy to more negative values with temperature increase from 303 to 323 K suggests that

Table 4
Thermodynamic parameters for catechol adsorption onto CTAB-B

Temperature ($^\circ\text{C}$)	ΔG° (kJ mol^{-1}) using Eq. (8)	ΔG° (kJ mol^{-1}) using Eq. (7)	ΔH° (kJ mol^{-1})	ΔS° ($\text{J mol}^{-1} \text{K}^{-1}$)
30	-12.186	-12.446 ± 0.094		
40	-12.596	-12.616 ± 0.196	-7.3 ± 0.148	16.985 ± 0.467
50	-12.797	-12.787 ± 0.199		
60	-12.957	-12.956 ± 0.203		

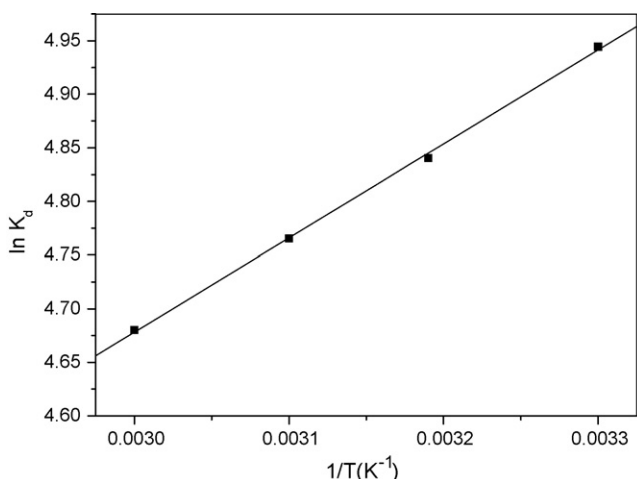


Fig. 9. $\ln K_d$ vs. $1/T$ (K) for catechol adsorption.

the adsorption process is more spontaneous at high temperatures. The positive value of ΔS° indicates increased randomness at the solid/solution interface during the adsorption process. Again, the negative values of ΔG° and ΔH° indicate that the adsorption process is exothermic which agrees well with the experimental observations (Fig. 7).

4. Conclusion

Cetyltrimethylammonium bromide-bentonite produced by the exchange of cetyltrimethylammonium cation for inorganic ions on surfaces of bentonite, was investigated for the removal of catechol contaminant from aqueous solutions. Removals obtained in the neutral and slightly acidic pH range, where catechol exists mainly as the neutral (non-charged) molecule, are relatively low and could be mainly related to van der Waals interaction between the neutral catechol molecules and the $-R$ groups of the quaternary ammonium ion. At $\text{pH} \geq 9.9$, where the catecholate anion predominates, the adsorption capacity is maximum (55.83 mg g^{-1}) and is attributed to favorable electrostatic interaction. The kinetic data could be properly described by the pseudo-first-order kinetic model and the intraparticle diffusion model. Both the Langmuir and Freundlich models fit well to adsorption data obtained (at 30, 40 and 50°C). The obtained enthalpy change (ΔH°) indicates exothermic adsorption and the positive value of ΔS° indicates increased randomness at the solid solution interface. The ΔG° values achieved at four different temperatures are negative indicating spontaneous physisorption process.

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