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Cadmium Adsorption on HDTMA Modified Montmorillionite

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امتصاص الكادميوم من المياه باستعمال المنتموريلونايت المعدله بواسطة HDTMA

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الخلاصة: في هذه الورقة تم بحث امكانية استعمال تربة المنتموريلونايت المعدله بال HDTMA لازالة الكادميوم من المياه عن طريق الامتصاص. التجارب الثابته التي تم اجراءها كشفت اته يمكن زيادة الكمية المزالة من الكادميوم بتعديل ١٠٠٪ من طاقة المنتموريلونايت التبادلية و ان الازاله تزداد بزيادة الرقم الهيدروجيني و ذلك نتيجة لترسيب الكادميوم على سطح المنتموريلونايت المعدل ثم تكوين مركبات. ازدياد الازاله هيضا هو نتيجه لتعادل شحنة المنتموريلونايت السالبة بشحنة ال HDTMA الموجبة. وجد ايضا ان المخطط الحرارى الانسب هو مخطط Langmuir مما يدل على التغطية ذات السطح الواحد. التجارب حققت طاقة امتصاص ٤٩ مغم/غم ونسب ازالة الى ٩٠٪.

المفردات المفتاحية: جودة البيئة، الامتصاص، المنتموريلونايت، ازالة الكادميوم.

Abstract: In this paper the possibility of cadmium removal from aqueous solutions by adsorption onto modified montmorillonite clay is investigated. Batch adsorption experiments performed revealed an enhanced removal of cadmium using HDTMA modified montmorillonite to 100% of its exchange capacity. Modified montmorillonite adsorption capacity increases at higher pHs suggesting adsorption occurs as a result of surface precipitation and HDTMA complex formation due to the fact that the original negatively charged montmorillonite is now covered by a cationic layer of HDTMA. Adsorption isotherms generated followed a Langmuir isotherm equation possibly indicating a monolayer coverage. Adsorption capacities of up to 49 mg/g and removals greater than 90% were achieved. Anionic selectivity of the HDTMA modified monmorillonite is particularly advantageous in water treatment applications where high concentrations of less adsorbable species are present, and the lack of organoclay affinity for these species may allow the available capacity to be utilized selectively by the targeted species.

Keywords: Environmental quality, Adsorption, Montmorillonite, Cadmium removal

1. Introduction

Inorganic pollutants from natural and anthropogenic sources are often found in drinking water. These pollutants include cadmium, lead, mercury, zinc, aluminum, chromium, cobalt, copper, nickel, and iron. The removal in order to of these pollutants should result in extremely low levels to comply with regulations. The conventional treatment sequence of coagulation-flocculation, sedimentation, filtration usually results limited removals of these compounds, which makes advanced treatment processes necessary. Activated carbon is used almost exclusively because of its high overall adsorption capacity when the removal of these compounds is desired (Najm, *et al*. 1991). Carbon adsorption is expensive, nonselective, adsorptive interference in the presence of naturally organic matter (NOM), competition effects of NOM are exacerbated with time, and it interacts with treatment chemicals.

Surfactant modified clays can provide selectivity, and are produced from inexpensive base material and are chemically regenerable. The absorption capacity of clay minerals have been shown to improve significantly due to the modification with quaternary ammonium compounds. The molecular structure of the modifying cations was also shown to play an important role in controlling the preference absorption and it could be concluded that modification of a specific clay mineral with a quaternary ammonium salt can produce a sorbent that is capable of sorbing inorganics from aqueous solutions (Barrer, *et al*. 1989; Barrer, *et al*. 1955). The sorption capacity of this modified clay can be maximized by the choice of appropriate surfactant.

Despite the fact montmorillonite have a large internal surface area, which can be as large as 800 m^2/g (Jamrah, *et al*. 1993; Ahmed, 1996) and is comparable to 1000 m^2/g for activated carbon (Weber, 1972), very few studies were carried out to evaluate the possibility of using these minerals for the treatment of water and wastewater from inorganic contaminants (heavy metals). Examples of these studies include the use of hexadeceltrimethylammonium (HDTMA) modified ziolite as an adsorbent for the removal of chromate and other inorganic anions (Haggerty, *et al*. 1994; Katsuhiko, *et al*. 2006). Most of

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*Corresponding author's e-mail: ahmemoh@iit.edu the adsorption studies that have been performed with clays have utilized the clay in its natural state, with no effort to improve the adsorptive capacity of the clay by pretreatment with other chemicals. The chemical treatment of the clay may be needed in some applications (Jamrah, *et al*. 1993; Ahmed, 1996). The major goal of this paper is to chemically modify naturally occurring Wyoming montmorillonite with quaternary amine salt (HDTMA). The objective of the chemical treatment was to improve the adsorptive capacity of montmorillonite.

2. Base Materials

Organo-clays are typically smectite clays in which the natural exchange cations are replaced by alkylammonium or quaternized cationic surfactant (Barrer, 1978). This substitution of organic cations changes the surface properties of the clay from strongly hydrophilic to organophilic and decreases the hydration of the clay as the aluminosilicate surface area of the mineral not covered by the organic exchange ions decreases. Further, these exchange ions act as pillars that hold the aluminosilicate sheets apart (Jamrah, *et al*. 1993; Ahmed, 1996).

Organoclay complexes have been utilized for many years (Brindley, *et al*. 1969). The clay used in this work, Wyoming montmorillonite, has been utilized in previous studies ((Jamrah, *et al*. 1993; Ahmed, 1996; Haggerty, *et al*. 1994; Katsuhiko, *et al*. 2006). It is also used as base materials in some commercially available organo-clays (*eg*. Bentones B27, B34, B38).

2.1 Montmorillionite

Montmorillonite is an aluminum dioctahedral smectite clay mineral. Based on the data presented in Table 1, it would appear that the different types of montmorillonite can be distinguished by their structural formulae.

Table 1. Reported structural formulae of Wyoming montmorilonite

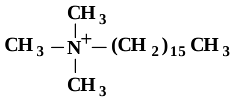
Formula	Source
$(Si^{+4}_{7.790}Al^{+3}_{0.210})(Al^{+3}_{3.070}Fe^{+3}_{0.400}Mg^{+2}_{0.490})O_{20}(OH)_4$	Foster (1953) [11]
$(Si^{+4}_{7.680}Al^{+3}_{0.320})(Al^{+3}_{3.050}Fe^{+3}_{0.420}Mg^{+2}_{0.520})O_{20}(OH)_4$	Earley *et al*. (1953) [12]
$(Si^{+4}_{7.710}Al^{+3}_{0.290})(Al^{+3}_{3.010}Fe^{+3}_{0.380}Fe^{+2}_{0.040}Mg^{+2}_{0.520})O_{20}(OH)_4$	Grim (1968) [13]

Wyoming montmorillonite, prior to use, was purified to achieve a size of < 2 µm by the process described elsewhere (Jamrah, *et al*. 1993). The Cation Exchange capacity (CEC) of the clay was measured using the method of Calcium-Magnesium exchange (Ahmed, 1996), and the CEC per unit mass of the clay was found to be 93.0 meq/100 grams of the dry clay.

2.2 Surfactant

The surfactant used in this study is hexadecyltrimethylammonium bromide, Table 2, which is a quaternary ammonium compound, which is a cationic surfactant that can be conveniently produced by reacting a suitable tertiary amine with an alkylating reagent. The reagent is usually an organic halide or organic sulfate. The hydrophobic group in the quaternary ammonium salts has a positive charge when dissolved, and thus adsorbs strongly onto negatively charged surfaces. Furthermore, this positive charge is not affected by the pH of the media, indicating that quaternary ammonium salts are stable, especially in acidic solutions 5.

Table 2. The cationic surfactant used in clay modification

Surfactant	Abbreviation	Molecular Weight (g)	Structure
Hexadecyltri-methyl-ammonium bromide	HDTMA	364.46	 $CH_3-N^{+}(CH_3)_2-(CH_2)_{15}CH_3$

3. Experimental Methods and Analysis

3.1 Batch Adsorption Experiments

All adsorption experiments were carried out using a standard batch procedure at room temperature (25^{o}C). First, the adsorbent was prepared in 50 mL borosilicate glass centrifuge tubes with Teflon-lined screw caps. Clay samples of 50 mg were weighed in each of the tubes (as determined from preliminary experiments described later), then the surfactant solutions were added in amounts sufficient to replace the desired percentage of the CEC. Although preliminary kinetic studies on HDTMA showed that the reaction was complete in 4-6 hours (Jamrah, *et al*. 1993), the tubes were then shaken on a rotary shaker (3 rpm) for a period of 16-24 hours. The clay suspension in the tubes was allowed to settle, and the separation of the phases was achieved by evaporation at room temperature.

Adsorption isotherms for the organo-clays were then generated, with cadmium using 200 mL flasks. Stock solution of cadmium was prepared, and added in the desired initial concentrations. Cadmium concentrations were measured before and after each pH adjustment. In the case of controlled pH experiments, the pH was period-

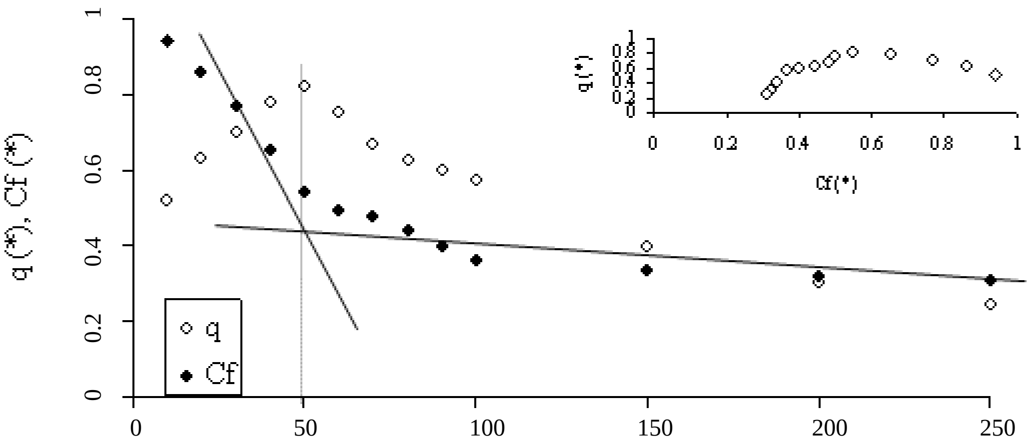


Figure 1. Normalized final cadmium concentration (C_f) and normalized solid phase concentration (q) as a function of the amount of clay mass used in 150 ml solution with 30 mg/l cadium

ically checked during the adsorption process and adjusted using buffer solutions; a minimal headspace was allowed to insure good mixing throughout the adsorption experiment. The flasks were shaken in a Gyrotory shaker model G33-B positive rotary motion shaker- (250 rpm). A reaction period of 18-24 hours was allowed, although preliminary kinetic experiments on cadmium showed that the uptake reaction was complete in 14 hours (Ahmed, 1996). Following the reaction period, the flasks were allowed to settle and samples were taken for analysis of residual aqueous concentrations. Phase separation was achieved by filtration using 0.45 µm membrane filters.

Sorption isotherms were generated using initial cadmium concentrations ranging from 5 to 30 mg/l. A total of 50 mg of modified montmorillionite and 150 mL of cation solution were placed in a 200-ml flasks. Sorption at 100% HDTMA loading (fully exchanged clay, (Haggerty, *et al*. 1994) was examined for variable pH ranges and the effect of pH variation on cation sorption was determined and will be discussed later. pH was measured before and after equilibrium.

3.2 Analysis

Samples were analyzed for cadmium concentration using a multiple ion meter (pX meter) model 925 (Fisher Scientific), which measures pH, voltage, temperature and ion concentration. The electrode used was an Orion combination electrode (sure-flow combination electrode model 9648), pH changes were accounted for in regard to the electrode potential behavior versus pH and limits of detection.

Prior to measurement of concentrations, samples were prepared in a 50 ml beakers after being filtered and adjusted for ionic strength. The ionic strength adjustment was done after the pH measurement, this is for the fact that the electrode performance depends solely on the use of ionc strength adjuster (5M $NaNO_3$, model 940011).

Both the standard electrode and ion-specific electrodes were immersed in sample beaker solution after connection to the pX meter. The pX meter was then allowed to stabilize its reading (5 to ten minutes) and give signal before reading is recorded.

4. Results and Discussions

4.1 Adsorption Isothrems

A study of the adsorption of cadmium onto modified montmorillonite as a function of the amount of adsorbent was first conducted to determine the optimum amount of clay (least ratio of amount of used clay to amount of removed cadmium) to be used in the following experiments. Figure 1 indicates that the final concentration decreases with increasing amount of clay added but the clay loading capacity increases to a certain extent after which clay loading decreases indicating that the clay used is much more than needed for the limited amount of cadmium available. This experiment yielded 50 mg of clay as the optimum adsorbent amount to be used for 150 mL solution, 30 mg/L initial cadmium concentration, and pH 6. Results in Fig. 1 are normalized to the maximum obtained adsorption capacity of clay and a maximum initial concentration of 30 mg/l.

Figure 2 shows cadmium adsorption isotherms at different pHs. The results shown are averages of two experiments and errors in these isotherms were in the 5% range. As indicated by Fig. 2 modified montmorillonite has a little affinity for cadmium ion Cd^{2+} (low pH) compared to other species Cd(OH)+, $Cd(OH)_2$, $HCdO_2^-$, CdO_2- consecutively in order (higher pHs), however the amounts of each, sorbed, cannot be determined exactly but can be arranged in the order of which is favorable. Also according to a study conducted by (Haggerty, *et al*. 1994) on the sorption of anions by organoclays he concluded that sorption of some anions that are present in the solution is favorable to some degree, and that might even be greater at medium pH ranges (5.8 to 7.5). Hence we can conclude

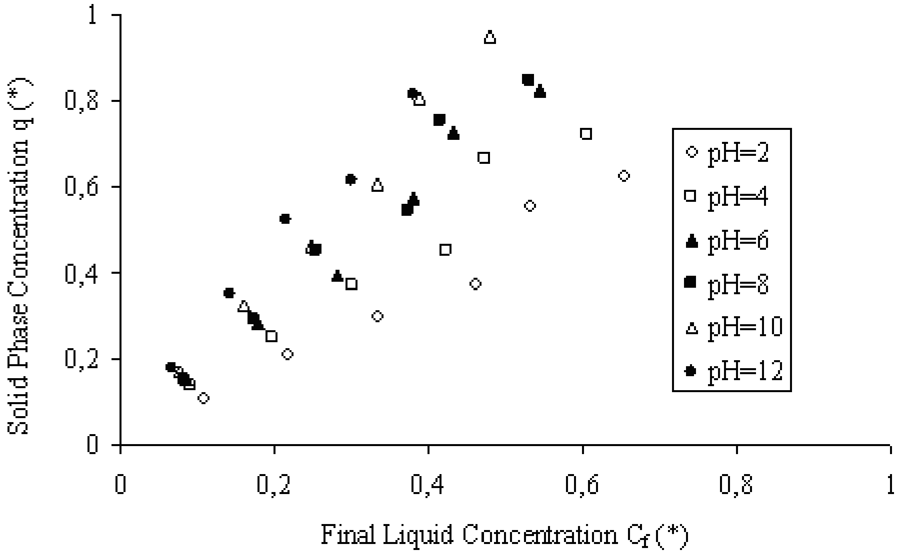


Figure 2. Cadmium adsorption isotherms at different pH's. Initial cadmium concentrations ranging from 5 to 30 mg/l. A total of 50 mg of modified montmorillionite and 150 mL of cation solution were placed in a 200-ml flasks

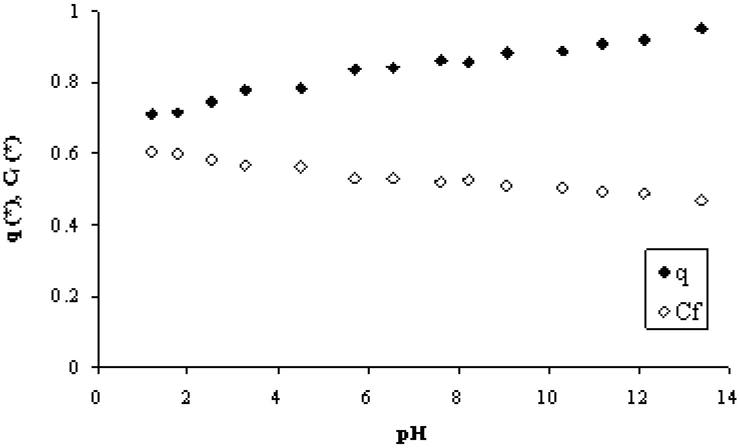


Figure 3. Adsorption of cadmium onto modified montmorillionite as a function of pH, (C_f) is the normalized final cadium concentration and (q) is the normalized solid phase concentration

for sure that at lower pH ranges sorption of cadmium cationic species is strong relatively (as we will see later that sorption of cadmium is generally weak specially below pH 6 where cadmium is present entirely as C^{d+}), and at higher pH ranges sorption of anionic species is strong.

Also at pH's greater than 2 the isotherms have a steeper slope that means the adsorptive capacity increases at higher equilibrium solute concentrations at these pH values, over that at lower concentration. That means, at higher pH values, in general, the modified clay is efficient for column application than at lower pH values. However, it must be emphasized that the performance shown by the isotherm is indicative only of the performance of the modified clay under the static isotherm test conditions. Additional column tests would have to be conducted to evaluate the performance of the modified clay in a continuous flow system.

The isotherm data of Fig. 3 can be described by a linear isotherm, a Freundlich isotherm, or a Lamgmuir isotherm equations as displayed by equations 1, 2, and 3 respectively (Weber, 1972):

$$q = KC_f \tag{1}$$

A Freundlich isotherm,

$$q = KC_f^{1/n} \tag{2}$$

Or a Langmuir isotherm [r]

$$q = \frac{aKC_f}{1 + aC_f} \tag{3}$$

Table 3. Adsorption isotherm fitting at different pH's obtained from Figure 2

Isotherm Type		**pH**					
		$pH = 2$	$pH = 4$	$pH = 6$	$pH = 8$	$pH = 10$	$pH = 12$
Linear	K	1.5771	2.0519	2.5759	2.7459	3.2704	3.7675
$q = KC_f$	R^2	0.963	0.9523	0.9827	0.9641	0.9865	0.9752
Freundlich	K	1.7638	2.833	2.9761	3.2223	3.7622	4.7909
$q = KC_f^{1/n}$	$1/n$	0.9524	0.8702	0.9373	0.9346	0.9354	0.8925
	R^2	0.9806	0.9753	0.9875	0.9853	0.9907	0.9896
Langmuir	a	0.011681	0.033632	0.019097	0.013501	0.021121	0.026598
$q = \frac{abC_f}{1 + aC_f}$	b	151.5152	83.33333	158.7302	232.5581	181.8182	175.4386
	R^2	0.9934	0.9842	0.9918	0.995	0.9945	0.9968

Where q is the sorbed mass per unit weight of adsorbent, C_f is the final equilibrium solution concentration, and K is the adsorption capacity, a is the Langmuir adsorption constant. The adsorption isotherms fitting at different pHs are given in Table 3. The linear equation is valid ideal solution conditions, which implies low solute concentration at which the solute is completely ionized and at equilibrium conditions.

The nonlinearity observed on the adsorption isotherms at higher solute concentrations (>20 mg/L) is mainly due to the violation of the assumption of monolayer adsorption of the linear isotherms.

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Langmuir's isotherm is based on the assumption that points of valency exist on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule; thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. Table 3 suggests a strong relationships is provided by all isotherms, however, the Langmuir is the best representation of the adsorption of cadmium onto HDTMA modified montmorillionite. This result conforms to the monolayer adsorption assumption underlying the Langmuir isotherm.

4.2 pH Effects

The pH of a solution from which adsorption occurs may, for many for one or more a number of reasons, influences the extent of adsorption. Because hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions is influenced by the pH of the solution. Furthermore, to the extent to which the ionization of an acidic or basic compound affects its adsorption, pH affects adsorption in that it governs the degree of ionization. Cadmium (Cd^{2+}) is present totally as the divalent species up to pH 8, in the absence of any precipitating anions such as phosphate and sulfide. Cadmium begins to hydrolyse at pH 9, forming $Cd(OH)^+$ species (Pourbaix, 1974). Higher hydroxy species of cadmium are not relevant at the pH values commonly found in the environment. Dominance of Cd^{2+} species in contaminated lakes is reported (Snoeyink, *et al*. 1980). Under the conditions of these studies, pH dependence was observed and the major portion of the cadmium was in the form of Cd^{2+} at low pHs and $CdOH^+$ at high pHs (>8) (Pourbaix, 1974).

Generally complexes of metal tends to sorb more strongly at clay surfaces than do the free metal ions (Ahmed, 1996). At pH values below 6, where the cadmium is present entirely as Cd^{2+}, there is very little adsorption, relatively. As the pH increases, the removal of cadmium from solution by adsorption on modified clay particles increases gradually. In the pH range 6 to 8.5 the Cd^{2+} ion decreases, and the predominant cadmium species become the adsorbable hydroxy-cadmium complexes,

Table 4. Minteqa2 speciation results of 150 ml of 30 mg/l Cd and 50 mg modified clay

pH	**Percent of Total Cadmium Bound in Species**				
	Cd^{2+}	$CdOH^{+}$	$CdOH_{2}^{o}$	$CdOH_{3}^{-}$	Cd^{2+} *Adsorbed*
2	91.9	0	0	0	8.1
4	87.3	0	0	0	12.7
6	85.8	0	0	0	14.2
8	84.4	0.6	0	0	15.0
10	41.0	30.9	19.2	0	8.8
12	0	1.0	59.3	39.6	0

$CdOH^{+}$, $Cd(OH)^{o}_{2}$. Presentation in Fig. 3 is to summarizes the adsorption of Cd(II) onto HDTMA modified Wyoming Montmorillionite, using pH as the master variable.

A geochemical equilibrium model (MINTEQA2 (Allison Geoscience Consultants, Inc, 2003)) was used to study the speciation of cadmium (30 mg/l) solution. The equilibrium pH was about 6.8 and mostly cadmium exists as a free ion. When the pH was fixed at 12 the speciation contained only hydroxyl species (59% $CdOH^{o}_{2}$ and 40% $CdOH_{3}^{-}$) and no solids precipitated and therefore at such low cadmium concentrations precipitation is not a removal mechanism. Also Minteqa2 geochemical equilibrium model was used to study the speciation of cadmium in solutions containing the modified clay (50 mg in 150 ml solution and 30 mg/l cadmium). The adsorption data were taken from Table 3 and the pH was fixed at the experimental values (2, 4, 6, 8, 10, and 12). The results of this modeling are shown in Table 4. The adsorption was assumed to be solely dependent on free cadmium ion, and therefore Table 4 can be used to infer upon the quantities of hydroxocomplexes adsorbed and adsorption nature. At pHs up to 8 cadmium exist solely as a free ion and the increase in adsorption capacity is attributed to clay behavior, while at higher pHs (10, 12) the formation of cadmium hydroxocomplexes increases significantly and surface reaction with clay is completely responsible for adsorption as in the case of pH 12.

There is a suggestion that the almost total metal removal at the alkaline pH region may be caused by chemical precipitation. However, results from adsorption experiments using metal concentrations well below the precipitation limit have produced the same effect (Haggerty, *et al*. 1994), and is included in this study. Therefore, it seems clear that even at moderately high concentrations *ie*. 10^{-5} to 10^{-4} M, an adsorption of the metal ions by the modified clay can prevent metal precipitaion from occuring. Moreover, adsorptive removal can only result in a less-than-monolayer coverage. This was observed in most metal adsorption experiments.

Both the rate and extent of adsorption by particles of a fixed size should vary approximately linearly with the dosage of adsorbent over a range of doses that do not result in great differences in the concentration of solute remaining in bulk solution phase 6. Large differences in the concentration of residual solute introduce a second variable for both rate and capacity for adsorption. However the particle size of the modified montmorillonite is very small in the order of 10^{-6} m^4, and this indicate the large surface area it has and that almost every pore is available for adsorption.

4.3 *Nature of the Adsorbate*

In any consideration of adsorption from solution one fact is immediately evident; the solubility of the solute is, to a large extent, a controlling factor for adsorption equilibria. The solubility of cadmium increases at higher pHs and therefore the adsorption capacity was higher. Haggerty, *et al*. 1994, suggested three mechanisms for adsorption of oxyanions on modified clays which are; 1) sorption by HDTMA admicelles; 2) Chemical reduction; and 3) surface precipitation and formation of HDTMA complexes. The first mechanism is excluded since the clay is rinsed with water after modification to remove excess surfactant. The second and third mechanisms are possible and confirm the increase of adsorption at higher pHs but the third is the likely mechanism since oxyanions can attach to the cationic end of the HDTMA on the montmorillonite surface. Only these qualitative data can be inferred from this discussion, however more detailed work is needed to confirm this conclusion.

5. Conclusions

In summary, this study has investigated an alternative sorbent (montmorillionite modified with HDTMA) that can be used in water treatment applications. However, although results presented herein are promising, more experimental work needs to be done especially to investigate leaching of HDTMA and bromide into the treated water, and reaction with disinfectants (chlorine and ozone) to form potentially harmful byproducts. The conclusions of this paper are:

1. The ability of modified montmorillonite to remove cadmium hydroxo-compounds from solution increased with pH due to the fact that organoclays removed the anionic species first, the modified clays were able to selectively remove these sorbates from water with no significant competition from other inorganic components of surface waters.
2. Adsorption isotherms at different pH values indicated that the hydroxo forms of cadmium were preferentially adsorbed on the modified montmorillionite, which suggested that surface precipitation and HDTMA complex formation might be the uptake mechanism.
3. The adsorption of cadmium ions onto modified montmorillionite was found to follow a Langmuir isotherm suggesting a monolayer coverage.

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