Restrictive Entry of Aqueous Molybdate Species into Surfactant Modified Montmorillonite—A Breakthrough Curve Study

N. Mahadevaiah,[†] B. Venkataramani,[‡] and B. S. Jai Prakash*[,†]

Chemistry Research Laboratory, Bangalore Institute of Technology, K.R. Road, Bangalore 560 004, India, and Analytical Division, Bhaba Atomic Research Centre, Trombay, Mumbai 400 085, India

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Molybdenum sorption behavior and the nature of breakthrough curves have been studied in a fixed-bed column containing montmorillonite clay modified by treatment with cationic surfactant hexadecyltrimethylammonium (HDTMA) bromide. Different amounts of the surfactant loaded into the interlayer region of the montmorillonite to increase the interlayer spacing is found to enhance molybdate sorption. The sorption was found to be at a maximum in acidic medium ($pH < 0$) and was almost constant between pH 3 and 4. Beyond pH 4, adsorption decreased rapidly and was almost two to four times lower than that in the acid medium. It is known from the equilibria of aquo molybdate species that polymolybdate species $Mo_8O_{26}^{4-}$ and $Mo_7O_{24}^{6-}$ are prevalent in the highly acidic medium; the species H_2MoO_4 and $HMoO_4^-$ are stable between pH 0 and 4, and MoO_4^{2-} is predominantly present above pH 5. The variation in adsorption of Mo is interpreted on the basis of the type of species prevalent at different pHs. The sample loaded at 0.5 CEC of surfactant with an interlayer spacing of 5.2 Å was found to adsorb negligible amounts of molydate, whereas that loaded with surfactant corresponding to 1.5 times its CEC is able to admit $HMoO_4^-$ and MoO_4^{2-} species into the interlayer of clay sheets but not the larger polymolybdate ones. The samples loaded with surfactant corresponding to 2.0 times its CEC swells enough (32 Å) to admit polymolybdate species $Mo_7O_{24}^{6-}$ (23.8 Å) and $Mo_8O_{26}^{4-}$ (27.2 Å). Shapes of breakthrough curves obtained at different surfactant loadings clearly support the restricted entry of the molybdate species. The study has demonstrated, for the first time, the possibility of sieving of the anionic species in the aqueous medium by carefully manipulating the gallery height of a layered material. Sorption energy calculated from the DKR equation shows that the interaction between the surfactant and molybdate follows an ion-exchange mechanism. Washing with dilute alkaline solution releases the molybdates quantitatively and regenerates the column material. The regenerated column material shows no change in the breakthrough curves when repeatedly used for molybdate adsorption.

Introduction

The phenomenon of adsorption is extensively used in industries for effective removal and recovery of variety of species from the medium. The most effective adsorbents for the removal of inorganic and organic species from aqueous environment and industrial effluents are activated carbons, silica gels, zeolites, diatomite, hydrous oxides, and montmorillonite clays.[1−3]

Clays are hydrated aluminosilicates characterized by the linking of silicate tetrahedral sheets with aluminate octahedral sheets in their structure. The unit formed by two tetrahedral sheets enclosing one octahedral sheet is referred to as a 2:1 type, and the resulting clay mineral belongs to the smectite group. An important smectite is the montmorillonite, which possesses a net negative structural charge resulting from isomorphous substitution of cations (for example, Al for Si in the tetrahedral sheet and Mg for Al in the octahedral sheet) in the crystal lattice. Aquocations of metals such as Na, K, and Ca balance these negative charges that occupy the region between two sheets called the interlamellar or interlayer. The interlayer can swell depending on the cationic species present. The aquocations in the interlamellar region are exchangeable with other cations, which confers on the clay a cation-exchange capacity (CEC) that commonly ranges from 0.7 to 1 meq per g of the montmorillonite clay. Smectite clays have been of scientific and technological interest because of their applications as ion-exchange materials, adsorbents, catalysts, modified electrodes, and inorganic/organic composite materials.[4]

One of the outstanding properties of swelling clays such as montmorillonite is the simultaneous incorporation of polar or ionic molecules into the interlamellar spaces along with the medium. There is a large amount of literature regarding the swelling of clay interlayer by the incorporation of quaternary ammonium salts.[5] Long-chain alkyl ammonium ions have technical applications because of their organophilic properties.[6] Complexes of montmorillonite clay with long-chain alkyl ammonium ions show high basal spacing related to the length of the carbon chain.[7] Reports on adsorption of

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* Corresponding author. E-mail: jprak27@yahoo.com.

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[‡] Bhaba Atomic Research Centre.

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alkyl ammonium compounds by clays have shown that clays take up in amounts exceeding the exchange capacity of the mineral and that the electroneutrality is maintained by simultaneous adsorption of anions.[8,9]

HDTMA bromide, a cationic surfactant, is a tetrasubstituted ammonium cation with permanently charged pentavalent nitrogen and a long straight alkyl chain that imparts a high degree of hydrophobicity to the clay surface.[10] The cationic surfactant can in turn hold anionic ligand groups, within the clay layers, providing an example of surfactant-immobilized chemically modified clay. Surfactant-immobilized interlayer species bound to clay can facilitate the admission of cations into the interlayer regardless of their sizes. Such an immobilization by HDTMA for trapping lead ions has been demonstrated successfully.[11]

Molybdenum is an important element in the production of alloy steels, lubricants, and chemicals. Water-quality investigations near several molybdenum mining sites and factories have shown dissolved molybdenum from 0.003 to 0.22 mg/L in groundwater with a range of 0.005−11.4 mg/L at sites downstream of mine discharge.[12] Sodium molybdate (Na_2MoO_4), a toxicant, is reported to be the predominant form of molybdenum in aquatic systems of pH >5.[13] Molybdenum adsorption on halloysite, nontronite, kaolinite, montmorillonite, and illite and by soils have been reported.[14−16] The incorporation of molybdenum into mesoporous alumino phosphate along with primary alkyl amine surfactants as template materials have been reported.[17]

In the present work, fixed-bed adsorption studies were performed on surfactant-modified montmorillonite clay to retain and recover molybdenum species. The objective was to achieve restrictive entry of aqueous molybdate species, on the basis of their size, into the clay interlayer through layer separation by loading different amounts of surfactant to control the gallery height.

Experimental Section

Materials and Methods. The clay mineral used in this study was swelling type smectite-rich clay from the Bhuj area of Gujarat, India, supplied by Ashapura Chemicals. It was further fractionated to get a sample with a mesh size of less than 75 μm, which essentially contained montmorillonite as characterized by X-ray diffraction and X-ray fluorescence spectroscopy. The X-ray purity of montmorillonite was 74%, and other contaminants were quartz (17%), feldspar (7%), TiO_2 (1.24%), Cr_2O_3 (0.02%), MnO (0.11%), NiO (0.01%), P_2O_5 (0.04%), and S (0.16%). The cation-exchange capacity (CEC) of the sample, as determined by the $BaCl_2$ method,[18] was 90 meq/100 g of the clay. The cationic surfactant used in this study for modification of the surface of clay was hexadecyltrimethylammonium (HDTMA) bromide (SD Fine Chemicals, India). Sodium molybdate was purchased from Loba Chemie, India. Distilled water was used to prepare the aqueous solution for the tests in this study. The variation in the pH of the resultant solution was adjusted using 0.5 N HCl and dilute ammonia solution.

Table 1. Column Properties and Adsorbent Characteristics of Different Surfactant Loaded Clays

	initial surfactant loading		
adsorbent and column properties	0.5 CEC	1.0 CEC	1.5 CEC
sorbent density (g/mL)	1.0931	1.0941	1.0971
surface area ($m^2\,g^{-1}$)	4.84	3.50	2.66
pore diameter (Å)	89.7	79.1	75.4
column diameter (cm)	3.0	3.0	3.0
column bed height (cm)	4.5	4.5	4.5

Preparation of Surfactant-Modified Montmorillonite Clay. Known amounts of HDTMA bromide ranging from 0.137 to 0.85 g of HDTMA corresponding to 0.5−2.0 CEC per g of the clay were dissolved in water and used to prepare the surfactant-modified clay. The clay sample (15.0 g) suspended in acetone was added to the aqueous surfactant solution and the resulting mixture of clay−HDTMA was mixed thoroughly using a magnetic stirrer for 60 min. The mixture was centrifuged and the residue was washed several times with acidified water to remove excess surfactant on the surface of the montmorillonite. The resulting modified clay was ground, sieved to obtain less than 2 μm, and finally dried at 105 °C in an hot air oven.

Characterization. Known weights of samples ranging from 10 to 15 mg were taken for X-ray analysis. The X-ray patterns were obtained using Philips PW 3710 diffractometer (Cu−Kα radiation, $\lambda = 1.542$ Å) for randomly oriented powder samples. A step size of 0.02° (2θ) was used with a time of 1 s per step.

Nitrogen adsorption−desorption measurements were conducted in liquid nitrogen temperature at 77 K using Nova 1000 Quantachrome for the analysis of BET surface areas and pore size distribution. All samples were preheated at 100 °C for 2 h before the measurement.

Flow Experiments. The HDTMA-modified clay slurry, containing ~12 g of the dried clay, was packed into a glass column with an inside diameter of 3 cm and height of 30 cm. The physicochemical features of the column and bed are given in Table 1. The sorbent in the column was washed with deionized water in a down flow fashion in order to rinse the adsorbent to equilibrate the particles before a column test was begun. The molybdenum solution of known concentration (pH adjusted) was continuously fed, from a reservoir, to the top of the column at a desired flow rate. The solution was allowed to flow through the glass column with a control valve. The column effluent was intermittently collected in a separate collector and the effluent concentration was estimated

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Table 2. Initial Loading of HDTMA and the Amount Sorbed by the Clay

HDTMA initial loading		HDTMA sorbed	
mg	CEC	meq g^{-1}	mg
135	0.5	0.271	73.1
270	1.0	0.987	266.5
405	1.5	1.12	301.9
540	2.0	1.17	317.2

Table 3. Basal Spacings (d_{001}) of Surfactant-Treated Clays

sample	surfactant initially loaded (in terms of CEC)	basal spacing d(001) (Å)
(a) montmorillonite clay (dried at 110 °C)		9.5
(b) HDTMA modified clay	0.5	14.5
	1.0	18.2
	1.5	32.6
	2.0	40.5
	3.0	40.5

spectrophotometrically using peroxide method[19] until the concentration of molybdenum in the effluent remained constant.

Results and Discussion

The amount of HDTMA sorbed between the montmorillonite layers at different initial surfactant loading with respect to CEC was measured by CH anlayser. The results are reported in Table 2. At higher loadings of HDTMA, the modified clay was found to retain increased amounts of HDTMA. The sample treated with an initial loading of surfactant equivalent to 1.0 CEC is found to retain almost all the added HDTMA, whereas those loaded with 1.5 and 2 CEC showed more retention than the CEC. Above 2 CEC, there was no increase in the amount of HDTMA retained.

Powder X-ray diffraction (XRD) patterns of the clay material resulting from intercalation of HDTMA showed a clear swelling of the interlayers (Figure 1). The interlayer spacing of the clay without modification was found to be 9.5 Å, which increased to 40.5 Å for beyond 1.5 CEC surfactant-loaded samples. The increased interlayer spacings are given in Table 3.

The pH dependence of Mo(VI)$_{aq}$ sorption on surfactant-modified montmorillonite clays demonstrate that the amount adsorbed, in general, was found to be maximum in high acid strengths but was almost the same in the acid medium from pH 0 to 4 and decreased with an increase in pH (Figure 2). Equations 1 and 2 represent the dissociation of molybdic acid in acidic and alkaline medium with pK_a values of 4.0 and 8.24, respectively.[20,21]

$$H_2MoO_{4(aq)} \rightleftharpoons H^+_{(aq)} + HMoO_4{}^-_{(aq)} \qquad (1)$$

$$H_2MoO_{4(aq)} \rightleftharpoons 2H^+_{(aq)} + HMoO_4{}^{2-}_{(aq)} \qquad (2)$$

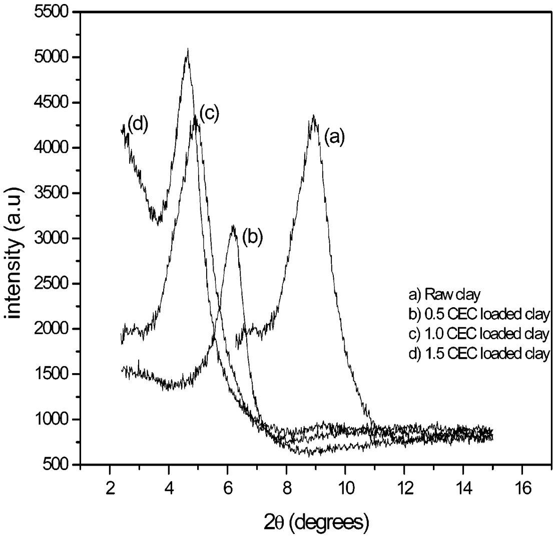

Figure 1. XRD patterns of raw clay and HDTMA loaded clays.

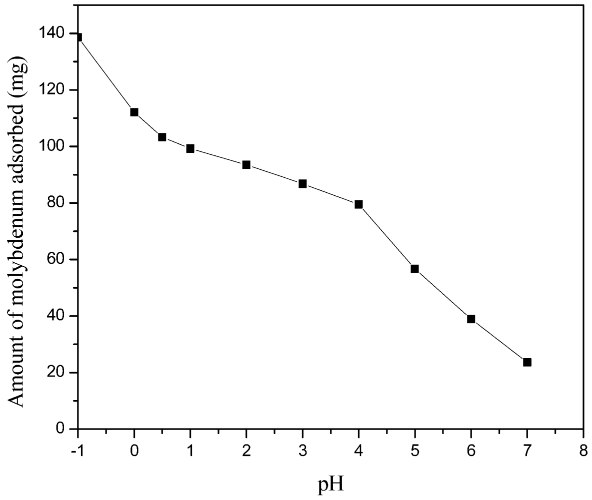

Figure 2. Effect of pH of the molybdenum solution on the adsorption by 1.5 CEC HDTMA-loaded clay.

Molybdenum species existing in alkaline solution (above pH 6) is the molybdate ion ($MoO_4{}^{2-}$). On such a solution being acidified, molybdate ions condense to form polymolybdate ($Mo_8O_{26}{}^{4-}$) and isopoly molybdate ($Mo_7O_{24}{}^{6-}$) ions.[14]

$$7MoO_4{}^{2-} + 8H^+ \rightleftharpoons Mo_7O_{24}{}^{6-} + 4H_2O$$

$$8MoO_4{}^{2-} + 12H^+ \rightleftharpoons Mo_8O_{26}{}^{4-} + 6H_2O$$

The overall equilibrium is given as

$$MoO_4{}^{2-} \xrightleftharpoons[\text{pH} >5]{\text{pH} <5} HMoO_4{}^- \rightleftharpoons Mo_7O_{24}{}^{6-} \rightleftharpoons Mo_8O_{26}{}^{4-} \rightleftharpoons \text{larger complexes}$$

One way to examine the entry of the various Mo(VI)$_{aq}$ species into the interlamellar region of the modified clays is to study the breakthrough curves at different pHs with surfactant-loaded samples expanded to different extents.

Breakthrough Curves. Experimental single solute breakthrough curves at a flow rate of 4.0 mL/min were obtained for molybdate sorption. Breakthrough data with respect to different initial surfactant loading (CEC) was acquired by plotting the ratio of m_e/v against time t (Figure 3) where m_e is the amount of molybdenum (mg) present in a volume v (mL) of the effluent collected at regular intervals of time (10 min). A pH of 1.5, where the predominant species are

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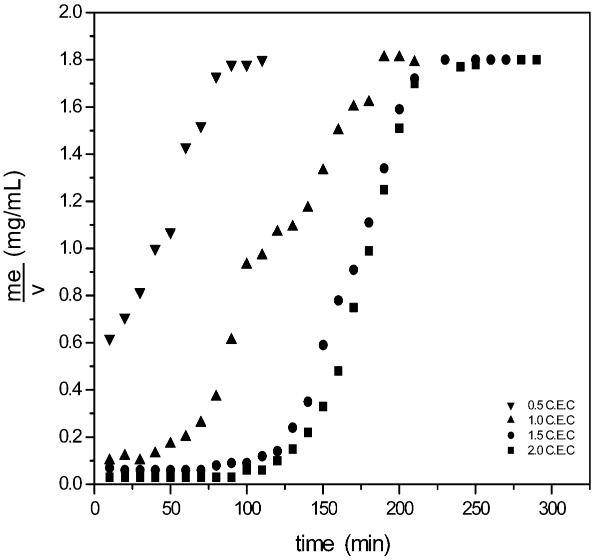

Figure 3. Breakthrough curves of molybdenum adsorption on clays at different surfactant loadings (pH 1.5 ± 0.1; inlet Mo concentration = 1800 mg/L).

Table 4. Experimental Conditions for Molybdenum Adsorption by Surfactant-Loaded Clays

initial surfactant loading (in terms of CEC)	0.5	1.0	1.5
weight of adsorbent (g)	12.0	12.0	12.0
pH of the molybdenum solution	1.51	1.49	1.53
concn of molybdenum in influent (mg/mL)	1.80	1.80	1.80
time interval for effluent collection (min)	10.0	10.0	10.0
flow rate of effluent (mL/min)	4.0	3.8	3.8

Table 5. Amount of Molybdenum Adsorbed for Different Surfactant-Loaded Clays (pH 1.0 ± 0.1, initial Mo concentration 1.82 mg/ml)

initial surfactant loading (with respect to CEC)	amount of molybdenum adsorbed	
	meq g^{-1}	mg g^{-1}
0.5	0.083	7.96
1.0	0.270	25.9
1.5	0.787	75.6
2.0	1.062	102

MoO_4^{2-}, was maintained for all preliminary experiments. The experimental conditions are presented in Table 4.

The nature of breakthrough curves of molybdate sorption at 0.5 CEC is indicative of negligible adsorption of molybdenum, possibly due to the narrow space available between the sheets (gallery height 5.2 Å) to interact with the surfactant. At 1.0 CEC loading, the interlayer space has increased to 9 Å, which is not enough for an easy entry of any of the molybdate species. The relatively distorted nature of the breakthrough curve obtained at 1.0 CEC loading demonstrates a forceful entry of the molybdenum species.

The nature of curve for 1.5 CEC surfactant loading, however, was typical of a breakthrough curve normally obtained for porous adsorbents. Interlayer spacing of 23.4 Å at 1.5 CEC loading permits the easy entry of the $HMoO_4^-$ and MoO_4^{2-} having a diameter around 3.4 Å. The spacing of 23.4 Å is somewhat less than the calculated size of the polymolybdate species (23.8 Å for $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$) and hence the latter, if present, would be restricted from entering. The amounts of molybdate adsorbed at each loading are given in Table 5. The maximum amount of Mo adsorbed at pH < 0 by the 1.5 CEC loaded clay was 89 mg.

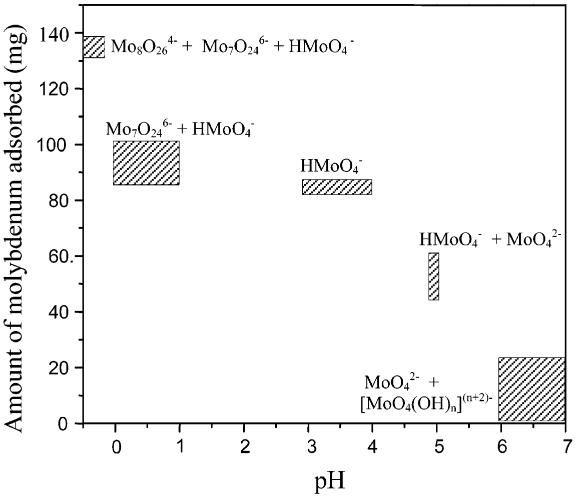

Figure 4. Effect of pH on the molybdenum uptake by 1.5 and 2.0 cec surfactant-loaded clays. Range of pH and the possible type of $Mo(VI)_{aq}$ anionic species based on the amount of Mo adsorbed are shown.

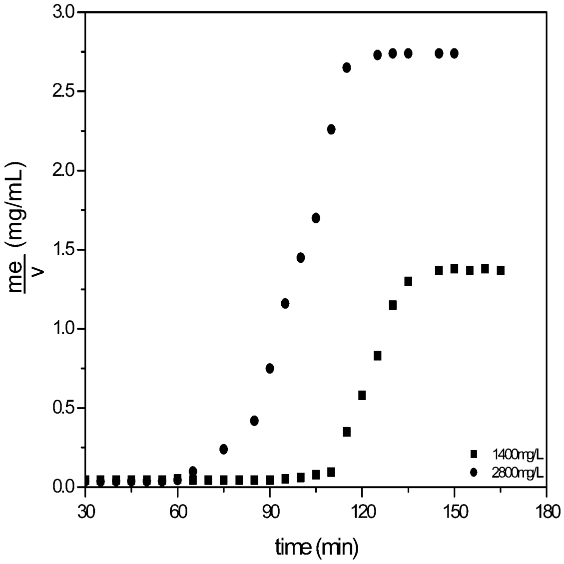

Figure 5. Breakthrough curves for molybdenum adsorption at different concentrations by 1.5 CEC surfactant loaded clay (pH 1.5 ± 0.1; inlet Mo concentration = 1400 and 2800 mg/L).

To facilitate the entry of the larger polymolybdate species, experiments were performed with modified clay loaded with 2 CEC surfactant having a basal spacing of 41 Å. In Table 6, the amount of Mo adsorbed and the predicted $Mo(VI)_{aq}$ species at various pH values based on the amount of molybdenum adsorbed at both the loadings are presented. The results were almost similar to those obtained with 1.5 CEC loaded clay for pH values above 6. At pH 5, both the clays always adsorbed between 43.2 and 86.4, which is attributed to the mixed and varying proportions of singly and doubly charged species, $HMoO_4^-$ and MoO_4^{2-}. Between pH 3 and 4, both of the clays adsorbed almost the same quantity of Mo (82−86 mg), demonstrating that the predominant species present between pH 3 and 4 are the mononegatively charged $HMoO_4^-$. In the presence of 2 and 4 M HCl (pH <0), the clay loaded with 2 CEC surfactant continued to adsorb molybdenum in greater amounts, whereas the 1.5 CEC loaded clay failed to do so. It is perhaps because of the fact that the polymolybdates are the predominant species at high acid strengths in addition to the singly charged

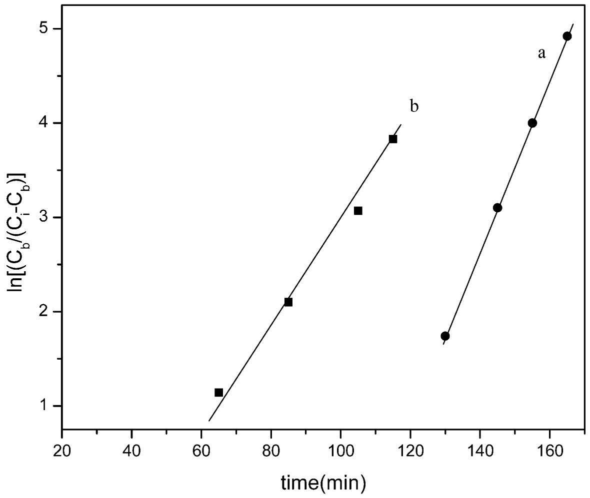

Figure 6. Yoon and Nelson parameters: plot of $\ln[C_b/(C_i - C_b)]$ versus time for the adsorption of molybdenum at two initial concentrations (a)-1400 (b) 2800 mg/L(pH 1.5 ± 0.1).

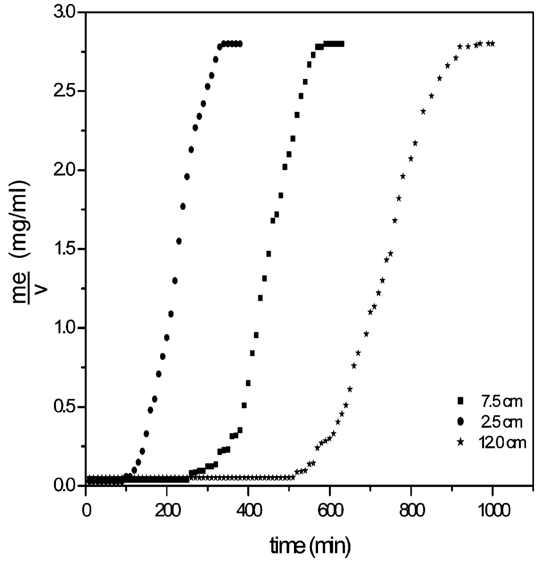

Figure 7. Effect of the bed depth on the breakthrough curve for 1.5 CEC surfactant-loaded clay (pH 1.5 ± 0.1; inlet Mo concentration = 2820 mg/L).

$HMoO_4^-$. The 1.5 CEC loaded clay with a interlayer spacing of 23.4 Å could not accommodate the larger polymolybdates, whereas the smaller $HMoO_4^-$ ions easily enter the interlayer of the 1.5 CEC loaded clay. The quantity of singly charged $HMoO_4^-$ for a 0.9 meq CEC clay would be 85 mg expressed as Mo. This may be the reason why the 1.5 CEC loaded clay shows a maximum adsorption of $HMoO_4^-$ corresponding to 85 mg of Mo even at pH <0, although other highly charged species are present. On the other hand, the 2 CEC loaded clay having a gallery height of 31 Å registers higher amounts of Mo at pH <0 for the reason that the predominantly available polymolybdates, because of their higher charge, preferably get into the interlayer relatively more easily. However, the amount of Mo adsorbed (123−139 mg, Table 6) is in between that calculated for $Mo_7O_{24}^{6-}$ (100.2 mg) and $Mo_8O_{26}^{4-}$ (172.8 mg), which shows that the ratio of the two polymolybdate species Mo_7:Mo_8 is approximately in the range of 1:0.845 to 1:1.03 at <0 pH values. Figure 4 illustrates the aqueous ionic species present at different pH values on the basis of the amount of Mo adsorbed.

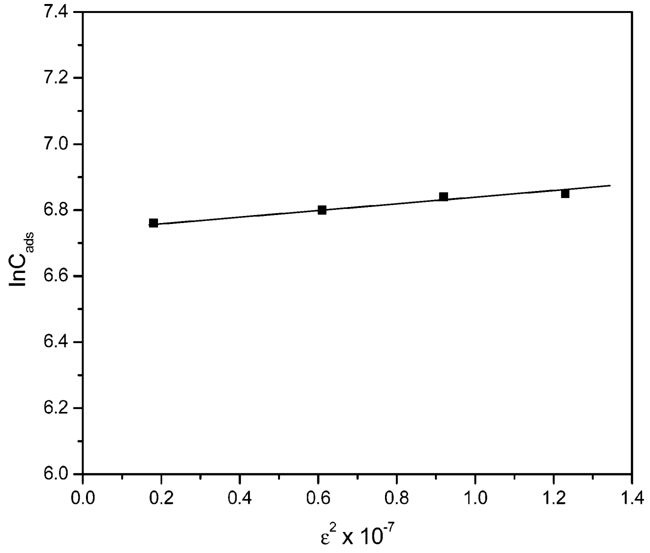

Figure 8. DKR parameters: plot of $\ln C_{ads}$ versus ϵ^2 for molybdenum adsorption by surfactant-modified clay.

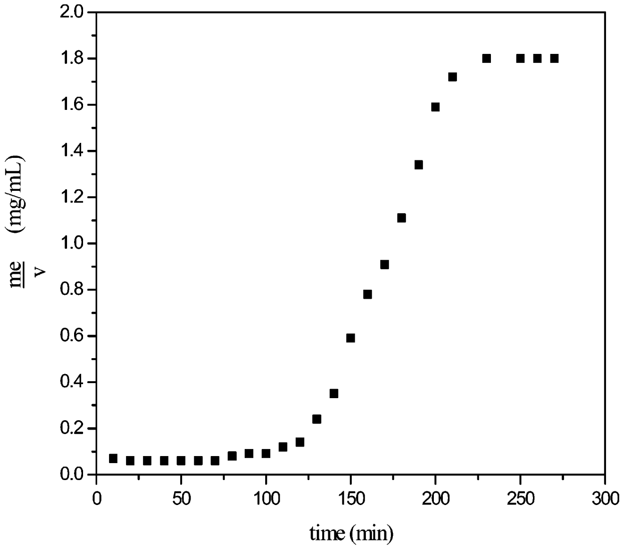

Figure 9. Breakthrough curve for readsorption of molybdenum on 1.5 CEC surfactant loaded clay after first regeneration (pH 1.5 ± 0.1).

Breakthrough Parameters. The breakthrough parameters at two initial molybdenum concentrations (1400 and 2800 mg/L) were determined. The experimental results, when plotted, show steep breakthrough curves (Figure 5). Curves show a decrease in the breakthrough time with the increase in the initial load of molybdenum: a 50% breakthrough time of 60 min for a higher concentration of 2800 mg/L and 118 min for a lower concentration of 1400 mg/L of molybdenum.

The Yoon and Nelson equation[22] is applied in this study to describe the 50% breakthrough time for adsorption of molybdenum on surfactant-modified clay at 298 K. Yoon and Nelson model may be mathematically expressed as

$$t = \tau + \frac{1}{\kappa'} \ln \frac{C_b}{C_i - C_b} \tag{3}$$

where t is the breakthrough (sampling) time, C_b and C_i are the breakthrough effluent concentration and inlet concentra-

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Table 6. $Mo(VI)_{aq}$ Species Predicted to be Present Predominantly at Various pH Values Based on Mo Adsorbed by 1.5 and 2 CEC Surfactant-Loaded Samples

predominant $Mo(VI)_{aq}$ species	calcd amount of Mo species for CEC = 0.90 (mg of Mo)	pH	amount of Mo (mg) actually adsorbed: 1.5 CEC loaded clay	amount of Mo (mg) actually adsorbed: 2 CEC loaded clay
$MoO_4^{2-} + [MoO_4(OH)_n]^{(n+2)-}$	0−43.2	>6	0−28	0−28
$HMoO_4^- + MoO_4^{2-}$	43.2−86.4	5	51	52
$HMoO_4^-$	86.4	3−4	82	86
$HMoO_4^- + Mo_7O_{24}^{6-}$	86.4−100.2	0.5−2	86−89	96−102
$HMoO_4^- + Mo_7O_{24}^{6-} + Mo_8O_{26}^{4-}$	86.4−172.8	<0	86−89	131−140

Table 7. Breakthrough Time from Breakthrough Curves and Yoon and Nelson Parameters for Adsorption of Molybdenum (pH 1.5)

		Yoon and Nelson parameters			
adsorbent	inlet concn (mg/L)	breakthrough time from breakthrough curves (min)	τ (min)	K' (min^{-1})	K
surfactant modified	1400	110	118	0.048	5.68
montmorillonite (1.5 CEC loaded)	2800	70	60	0.094	5.47

Table 8. Experimental Conditions for Molybdenum Adsorption at Different Depths of the Adsorbent

	height of bed depth (cm)		
experimental conditions	2.5	7.5	12.0
surfactant loading (in CEC)	1.5	1.5	1.5
pH of the molybdenum solution	1.56	1.51	1.54
initial concn of molybdenum (mg/mL)	2.82	2.82	2.82
flow rate of effluent (mL/min)	3.6	3.4	3.6

Table 9. DKR Parameters: Adsorbent Capacity (C_m), Adsorption Energy Constant (β), and Sorption Energy E for Molybdenum Adsorption by Surfactant-Modified Clay

DKR constants	adsorption of molybdenum on modified clay (1.5 CEC loaded)
C_m (mmol kg^{-1})	867.4
β ($mol^2\ J^{-2}$)	0.076×10^{-7}
r (correlation factor)	0.999
sorption energy, E (kJ mol^{-1})	8.11

tion, respectively, τ is the time required for 50% adsorbate breakthrough, k is the rate constant and κ', a proportionality constant that is equal to $k\tau$. The values of κ', k, and t have been calculated (Table 7) from the slope and intercept of the linear plots obtained by plotting ln $C_b/(C_i - C_b)$ versus t (Figure 6). Good agreement was found between the experimentally determined breakthrough parameter and those calculated on the basis of eq 3.

Column experiments for 1.5 CEC surfactant-loaded clay was also studied with respect to different bed depths. The experimental conditions are shown in Table 8. Both the sorption and breakthrough times increased with the increase in bed depth (Figure 7).

DKR Adsorption Isotherm Constants and Sorption Energy. The Dubinin−Kaganer−Rudushkevich (DKR) isotherm explains multilayer formation in microporous solids. The DKR equation confines to the monolayer region in micropores and has been widely used to explain energetic heterogeneity of solid surfaces at low coverages.

The DKR isotherm has been used to describe the adsorption of molybdenum on modified clay. The DKR equation has the following form[23]

$$\ln_{C_{ads}} = \ln_{C_m} - \beta\epsilon^2 \qquad (4)$$

where C_m is DKR monolayer capacity, β is a constant related to sorption energy, and ϵ is Polanyi potential that is related to equilibrium concentration as

$$\epsilon = RT \ln\left(\frac{1}{C}\right) \qquad (5)$$

where R is the gas constant in J K^{-1} mol^{-1}, T is the temperature in kelvin, and C is the equilibrium concentration of adsorbate. A linear relation is obtained on plotting ln C_{ads} against ϵ^2 (Figure 8). With linear regression analysis, the slope of the line gives β ($mol^2\ J^{-2}$) and the intercept yields adsorption capacity, C_m (mmol g^{-1}). The value of β is related to adsorption energy, E, via the following relationship given by Hobson[24]

$$E = \frac{-1}{\sqrt{-2\beta}} \qquad (6)$$

The correlation factor (r) and sorption energy (E) of molybdenum on modified clay are shown in Table 9. The correlation factor (ρ) is close to unity and the E value is 8.11 kJ mol^{-1} at 298 K. These values are on the order expected of an ion-exchange mechanism,[25] showing that the adsorption of molybdenum is possibly due to an ion-exchange process. The counterion of anionic molybdate species would exchange for the cationic HDTMA species neutralizing the negative layer charge. The adsorption capacity C_m at the DKR region is calculated to be 0. 867 mmol g^{-1}. Similar observations have been made on chromate and lead adsorption on HDTMA clay and Cu^{2+}, Zn^{2+} sorption on montmorillonite modified with dodecyl sulfate.[11,26]

Bed Regeneration. The adsorbed molybdenum species in the fixed-bed column was recovered by passing dilute ammonium hydroxide. Ammonium hydroxide at concentrations higher than 1×10^{-8} M releases all types of molybdenum species from the bed. The time and volume of dilute ammonia needed to elute the molybdenum species

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(24) Hobson, J. P. *J. Phys. Chem.* **1969**, *73*, 2720.

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completely does not vary with the concentration of the molybdenum species adsorbed. The column after the recovery of Mo is regenerated by a simple washing with dilute HCl. This can be repeatedly used several times for readsorption of molybdate. The nature of breakthrough curves after repeated sorption−desorption experiments were found to be similar (Figure 9). Further work is in progress to separate the aqueous molybdate species one by one using the same column containing different surfactant-modified clays designed to hold the respective species.

Conclusions

The variation in the gallery heights of montmorillonite clays by the incorporation of alkyl amines can be advantageously utilized for trapping cationic species based on their size and charge. The present work has demonstrated, for the first time, the restrictive admission of aqueous species of Mo(VI) into the interlamellar region of montmorillonite clay expanded to different extents. The nature of breakthrough curves is indicative of the restrictive entry of the species, and the DKR isotherm studies support the ion-exchange mechanism. The study has not only substantiated the usefulness of carefully altering the gallery height of a layered material to preferentially retain aqueous species on the basis of size and charge but also offers a method of verifying the aqueous chemistry of metal ions and their relative amounts in different conditions such as pH. The study suggests a new possibility of isolating a desired colloidal species by carefully fine-tuning the gallery heights through the incorporation of different ionic surfactants with varying chain lengths and high affinity for the species.

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