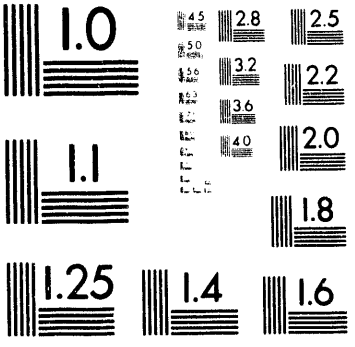
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DE-FG22-91PC91295

A NOVEL, INTEGRATED TREATMENT SYSTEM FOR COAL WASTE WATERS:

QUARTERLY REPORT:

FOR THE PERIOD March 2, 1993 - June 1, 1993.

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ABSTRACT:

The aims of this study are to develop, characterize and optimize a novel treatment scheme that would be effective simultaneously against the toxic organics and the heavy metals present in coal conversion waste waters. In this report, the following findings have been reported and discussed. Hec-CBDA-PA, (HCPA), a modified hectorite containing a mixed bilayer of a cationic (CBDA) and a long chain carboxylic acid (palmitic acid, PA) type surfactants, has been shown to adsorb Cu (II) strongly at pH 6.0 and quantitatively desorb the Cu(II) ions at pH 3.0. The overall mass balance of the adsorption/desorption cycle was quantified and it was found to be between 95 and 107%. Thus, a reversible, batch-wise scheme for the removal and recovery of a cationic heavy metal has been demonstrated. Future plans include repeated operation of the adsorption/desorption cycle. Adsorption of Cr(VI) onto HCDT and MONT-DT at pH 4.5 in presence and in the absence of a potentially competing organic ligand, β-naphthoic acid (NA), shows a limited amount of inhibition of Cr(VI) adsorption by NA. Further, the limiting adsorption density of Cr(VI) on the two adsorbents was found to be nearly the same (2.5 - 3.0 mmoles/g), and this value was considerably higher the surface concentration of DT (0.72 and 1.44 mmoles of DT/g adsorbent in the case of HCDT and MONT-DT respectively), which is the active component in the adsorption process. The excess adsorption is postulated to arise from the oxidation of surface organic carbon by Cr(VI) and the precipitation of Cr(III) as its hydroxide at pH 4.5. Adsorption of NA onto HCDT and MONT-DT as a function of pH in the 4.5 - 9.0 range shows that anion exchange and hydrophobic partitioning are the two dominant mechanisms of NA adsorption onto modified-clays.

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I. INTRODUCTION:

In our previous reports (1,2,3,4,5,6), we showed that a number of clay complexes can be prepared by a novel mixed bilayer approach, designated by us as the hydrophobic attachment method (HAM). In this method, the smectitic clay was first treated upto a monolayer (or the charge equivalence point) with a quaternary ammonium surfactant CBDA, a treatment that imparted hydrophobicity to the resultant clay. Subsequent attachment of an alkyl diamine (DT) or a long-chain carboxylic acid (palmitic acid, PA) by hydrophobic interaction between the alkyl chains of CBDA and those of DT or PA yielded a mixed bilayer on the clay surface and such clays were shown to be quite effective in reversibly adsorbing cationic heavy metals such as Cu(II) and Cd(II).

A second approach was to directly attach the protonated form of the diamine to the negative sites of the clay layer to form a bilayer. This approach, designated as the direct attachment method (DAM), was slightly less effective than the sequential treatment scheme mentioned above for the adsorption of cationic heavy metals such as Cu(II) and Cd(II). However, in our previous report (5) we have shown that both methods of attachment were effective in reversibly adsorbing anionic Cr (VI).

In an earlier report (4), we compared the relative effectiveness of two analogs of diamine surfactants: The water-soluble, Duomac-T (DuT), and the water-insoluble, Duomeen-T (DT). Duomac-T (DuT) is prepared by reacting DT with acetic acid to convert the amine group to ammonium, thus making DuT water-soluble (6). Our data revealed that DuT modification of hectorite-CBDA (Hec-CBDA) to form Hec-CBDA-DuT was ineffective with respect to Cu(II) adsorption. It was pointed out that the failure in this case might have arisen from the leaching of DuT coating on hectorite-CBDA-DuT by successive washings with deionized water. Alternatively, CBDA might have been displaced by DuT during the treatment of Hec-CBDA by DuT.

In summary, we have amply demonstrated that the pH of the continuous phase could be used as a " switch" to adsorb/desorb cationic and anionic heavy metal ions from most, if not all, of the clay complexes prepared as a part of this study.

A list of the five modified-clay complexes that have been prepared as a part of this study is as follows:

(1)	Hectorite-CBDA-Duomeen T:	(Hec-CBDA-DT, HCDT, the diamine type)
(2)	Hectorite-CBDA-Palmitic Acid:	(Hec-CBDA-PA, HCPA, the carboxylic acid type)
(3)	Montmorillonite-Duomeen T:	(MONT-DT, the diamine type in which the functional moiety is directly attached to the clay surface)
(4)	Montmorillonite-CBDA-DT:	(Mont-CBDA-DT, similar to Hec-CBDA-DT).
(5)	Hectorite-CBDA-Duomac-T:	(Hec-CBDA-DuT, similar to Hec-CBDA-DT, but containing the water-soluble, ammonium form of the diamine surfactant).

Our studies so far indicate that the mechanism of Cu(II) adsorption is of specific nature onto HCDT. This was verified by the appearance of a ligand to metal charge transfer

(LMCT) band at 626 nm in the spectrum of Cu(II)-DT complex in solution. Further, it was observed that adsorption of Cu(II) onto HCDT or MONT-DT imparted a blue color to the adsorbent. Similar color change was observed when Cu(II) adsorbed onto hec-CBDA-Palmitate, HCPA. However, increasing concentrations of 1:1 electrolytes in solution modified the adsorption of Cu(II) ions onto HCPA. A significant decrease in the affinity of adsorption with only a minor decrease in the limiting adsorption capacity were noted. Thus, it was concluded that adsorption of Cu(II) on HCPA was partly electrostatic and partly of specific nature.

We have also initiated a study on the adsorption of ionogenic organic compound, β-naphthoic acid, (NA), as a probe of the surface charge density of the surfactant-modified clays as a function of pH. β-naphthoic acid has a pKa of 4.17, and its mode of adsorption was expected to be a combination of anion exchange, hydrophobic partitioning and H-bond interaction. Preliminary results have been described and discussed (6).

In the present quarterly report, we will discuss the results from:

- The study of adsorption (removal) and desorption (recovery) of Cu(II) ions from solution using hec-CBDA-PA, HCPA as the sorbent. The adsorption and the desorption isotherms were measured respectively at pH 6.0 and 3.0. The overall mass balance of the adsorption/desorption cycle was quantified.

- Adsorption of Cr(VI) onto HCDT and MONT-DT at pH 4.5 has been measured in presence and in the absence of a potentially competing organic ligand, β-naphthoic acid (NA).

- Adsorption isotherms of NA onto HCDT and MONT-DT at pH 4.5 - 9.0 have been determined to establish the mechanism of NA adsorption onto modified-clays.

II. Adsorption/Desorption of Cu(II) from HCPA:

The preparation of HCPA has been described in one of our earlier reports (3). The relevant properties of HCPA are:

(1) Total wt % of adsorbed Surfactant: 36.0

(2) Surface Conc. of Palmitic Acid (PA) Groups: 0.56 mmoles/g

A slurry of HCPA (1 mg/ml; pH 6.0 and ionic strength 20 mM) was contacted with increasing concentrations of Cu(II) ions ranging from 1.1 - 30 mg/L. Positive controls and blanks were included to obtain an overall mass balance. After 20 hrs of equilibration, the adsorbent slurry and the control solutions were each filtered through a 0.20 μm hydrophilic Millipore membrane in an identical manner to separate solid and liquid phases. The solution was assayed for residual Cu(II) concentration.

Each membrane was then contacted with an equal volume of solution at pH 3.0 at an ionic strength of 20 mM. The intense blue color characteristic of Cu(II) adsorption onto HCPA faded instantly, but desorption was continued for 20 hrs. The slurry and the control solutions were filtered once more as the concentration of Cu(II) ions in solution at pH 3.0 was measured.
Figs 1 and 2 show the results of Cu(II) adsorption onto and desorption from HCPA.

Fig. 1 Adsorption/Desorption of Cu(II) on HCPA

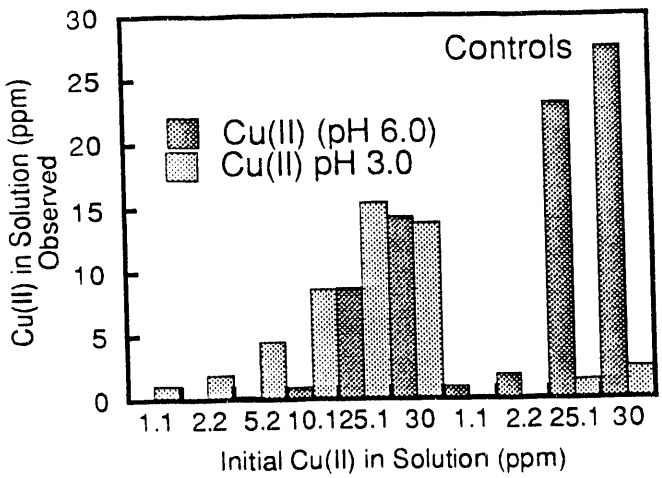
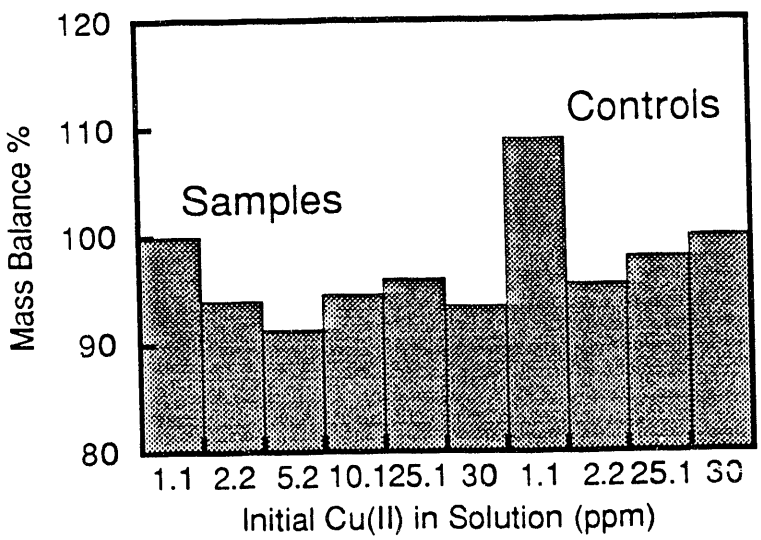


Fig. 2 Adsorption/Desorption of Cu(II) on HCPA: Mass Balance



The following observations can be made from Figs. 1 and 2.

(1) At low initial Cu(II) concentrations, adsorption at pH 6.0 leads to total depletion of metal ions from solution. On the other hand, control solutions show very little loss at pH 6.0. Thus, Cu(II) ions are shown to adsorb at pH 6.0. This is further verified by the intense blue color of Cu(II)-laden HCPA at this pH.

(2) At pH 3.0, the adsorbed Cu(II) is washed out of HCPA and is recovered in the solution at this pH. The amount recovered from control solutions is minimal and is attributed to possible adsorption to the filter membrane.

(3) The overall mass balance (the sum of Cu(II) concentration in solution at the two pH divided by the initial concentration) ranges from 95 to 107 %, thus providing

confidence and validity to the measurements reported here. Thus, it appears that modified-clays can be used to adsorb and desorb cationic metal ions **quantitatively** using pH shift as a " switch ".

III. Adsorption of Cr(VI) onto MONT-DT and HCDT:

The preparation of MONT-DT and HCDT have been described previously. The relevant properties are:

Modified-Clay	Wt% surfactant (Total)	Surface Groups (DT) (mmoles/g)
MONT-DT	50.4	1.44
HCDT	46.9	0.72

Adsorption of Cr(VI) was carried out at pH 4.5 using 20 mM Na acetate/acetic acid buffer system at a sorbent concentration of 0.25 mg/ml. Initial concentration of Cr(VI) ranged from 1.0 to 100 ppm. Residual Cr(VI) concentrations were by AAS (upto 10 ppm) and by absorbance at 350 nm (from 10 - 100 ppm). Controls were used to evaluate mass balance and to account for non specific losses, if any. Following equilibration, phase separation was achieved by filtration through a 0.20 μm filter.

A separate Cr(VI) adsorption experiment in presence of 20 ppm NA was also carried out under identical solution conditions to quantify the extent of competitive inhibition, if any, of Cr(VI) adsorption by NA. It should be noted that NA has a pKa of 4.17 and, therefore, about 60% of NA in solution will be in the anionic form and may be expected to bind competitively onto HCDT or MONT-DT.

The results are shown in Figs 3 and 4.

Fig. 3 Adsorption of Cr(VI); pH 4.5

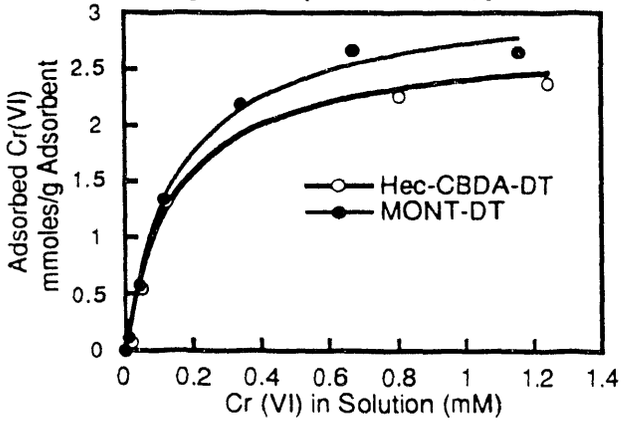
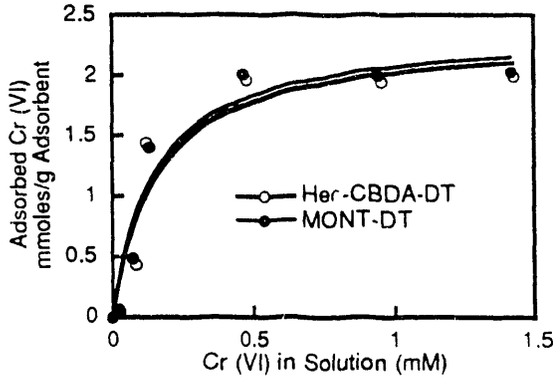


Fig. 4 Adsorption of Cr(VI); pH 4.5 In Presence of 2-naphthoic Acid



It can be seen that adsorption of Cr(VI) follows a similar profile on both HCDT and MONT-DT (Fig. 3). The limiting nature of adsorption suggests site-specific binding, and the data from Figs. 3 and 4 were fitted to a Langmuir type equation of the form:

$$q = q_0 K_a [C] / (1 + K_a [C]) \quad (1)$$

Where,
- q adsorbed amount (mmoles/g adsorbent)
- q_0 limiting Adsorption capacity (mmoles/g adsorbent)
- K_a Affinity Constant (mM^{-1})
- $[C]$ Equilibrium Solution Conc. of Cr(VI)

The relevant constants are tabulated in Table 1 for the two cases.

Table 1 Adsorption of Cr(VI) onto Modified-Clays:

Modified-Clay	K_a (mM^{-1})	q_0 (mmoles/g)	r^2 of the fit
MONT-DT	6.1	3.17	0.997
MONT-DT (with NA)	6.7	2.39	0.971
HCDT	6.5	2.78	0.987
HCDT (with NA)	6.4	2.34	0.952

The above table shows the following:

(1) HCDT and MONT-DT have similar adsorption affinities for Cr(VI). This is not surprising in view of the fact they have the common functional element, DT, at the solid-liquid interface.

(2) Langmuir-type plot is a reasonable depiction of the adsorption process.

(3) Presence of 20 ppm (0.12 mM) of β-naphthoic acid(NA) has no effect on binding affinity, probably because Cr(VI) is a divalent anion compared to the monovalency of NA. It should be noted that the buffer contains acetate ions at 20 mM.

(4) The limiting adsorption capacity is nearly the same for HCDT and MONT-DT, even though MONT-DT has twice as many surface DT groups as HCDT. Secondly, the limiting capacity is at least 2-3 times larger than the amount of DT groups on the surface of the two adsorbents.

A possible explanation is that Cr(VI) ions oxidize the surface organic carbon according to the following reaction at pH 4.5:

$$C + CrO_4^{2-} + 4H^+ = Cr(III) + 2\,H_2O + CO_2 \quad (2)$$

The resultant Cr(III) ions may precipitate out of solution as $Cr(OH)_3$. The above reaction has been invoked as a mechanism of Cr(VI) adsorption on carbonaceous materials such as peat and activated carbon (7, 8).

The above mechanism is supported by the fact that HCDT and MONT-DT have nearly the same amount of surface organic carbon in the form of adsorbed surfactant. This may

explain why the limiting adsorption capacity is nearly the same. The above reaction may also explain why NA had a minor effect on Cr(VI) uptake.

However, it should be noted that reaction (2) will be slower at higher pH and, while it may be faster at lower pH, the Cr(III) that is formed will be more soluble in aqueous medium, and thus reduce Cr uptake. Thus, we plan to re-examine pH dependence of Cr uptake by modified-clays.

IV. pH dependence of β-naphthoic acid (NA) uptake by modified-clays:

Adsorption of NA by HCDT and MONT-DT was carried out at pH 4.5, 7.0 and 9.0 using the procedure identical to the one used for Cr(VI) uptake studies. The ionic strength and the buffer systems used were:

pH	Buffer System and Ionic Strength
4.5	Na acetate/acetic acid; 20 mM
7.0 and 9.0	Tris (hydroxy methyl) amino methane/HCl, 20 mM

The initial concentration of NA was varied from 1.0 - 50 ppm (0.0058 - 0.29 mM). The residual NA concentration was assayed fluorimetrically using 287 nm excitation and 360 nm emission. Separate calibration curves were prepared at each pH. The fluorescence intensity of standards (in arbitrary units) was fitted to 3-degree polynomial and the actual sample concentration of NA was determined only by **interpolation**, diluting the solution, if necessary, to be within the interpolation range. Controls were used to obtain a mass balance on NA.

The data produced Langmuir type adsorption plots which were fitted to Langmuir adsorption equation (equation (1)) and the results are displayed in Table 2.

Table 2. Adsorption of NA by Modified-Clays: Langmuir Constants as a Function of pH.••

Adsorbent	Binding Constant $(mM)^{-1}$ pH			Limiting Capacity (mmoles/g adsorbent) pH		
	4.5	7.0	9.0	4.5	7.0	9.0
HCDT	241.1	32.2	2.7	0.69	0.93	0.61
MONT-DT	157.0	39.0	10.1	0.72	0.81	0.34

•• The correlation coefficients for the fitted data ranged from 0.96 to 0.993

The affinity of NA for the two modified-clays is high and decreases with increasing pH. Thus, anion exchange appears to be the dominant mechanism of adsorption of NA. The binding constant is much higher at pH 4.5 than at 7.0, which means electrostatic contribution to the adsorption process is significant. However, the limiting capacity has a maximum at pH 7.0 for both the adsorbents, and this indicates that the adsorption capacity is jointly controlled by the degree of deprotonation of NA and the positive charge of the adsorbent.

On the other hand, HCDT, which has a lower amount of DT on its surface appears to have a higher binding affinity and saturation capacity. Both HCDT and MONT-DT have nearly the same amount of surfactant on the surface. Thus, it would seem that hydrophobic partitioning of NA onto modified-clays may be equally important.

It should be noted that, unlike Cr(VI) uptake, the highest limiting adsorption capacity value of 0.93 mmoles of NA/g adsorbent (in the case of HCDT at pH 7.0) is below the actual capacity of HCDT, which will be 1.44 mmoles of monovalent charge /g HCDT. Thus, it would appear that only about 60% of the DT molecules on HCDT surface are protonated at pH 7.0. This will explain why Cu(II) ions are able to bind specifically to HCDT at this pH.

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(6) Henry Y. Wang and Keeran R. Srinivasan: VI Quarterly Report, DOE/PETC, March 1993.

(7) C. P. Huang and M. H. Wu: Water Research, **11**, 673 (1977).

(8) D. C. sharma and C. F. Forster: Water Research, **27(7)**, 1201 (1993).

VI. Publications

(1) On the Use of Modified-Clays for the Removal and Recovery of Heavy Metals From Waste waters:
Keeran R. Srinivasan and Henry Y. Wang
Proc. of the Joint International Meeting of the American and The Canadian Societies of Civil Engineering to be held in Montreal, Quebec, Canada, July 12 - 14, 1993. (In press).

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