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A NOVEL, INTEGRATED TREATMENT SYSTEM FOR COAL WASTEWATERS:

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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 wastewaters. 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. Increasing concentrations of NaCl reduce the affinity of Cu(II) adsorption onto HCPA. For example, the binding constants for Cu(II) adsorption onto HCPA at pH 6.0 are 88 and 35 mM⁻¹ at 20 and 200 mM NaCl respectively. The saturation binding capacity is also observed to decrease from 0.25 to 0.12 mmols Cu(II)/g adsorbent in the same ionic strength range. Spectral properties of Cu(II)-DT complex have been examined. Our previous results had shown that DT, an alkyl diamine, binds Cu(II) strongly at pH 7.4, but very weakly at pH 3.0. The formation of Cu(II)-DT complex at pH 7.4 produces an intense blue color and spectral measurements at 626 nm reveal a stoichiometric ratio of 3:1 for the DT-Cu(II) complex. β -naphthoic acid, a organic acid (pKa = 4.17), has been used to probe the pH dependent surface charge of montmorillonite-DT (MONT-DT) complex. Our results indicate that bulk of the surface diamines are de-protonated above pH 9.0.

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I. INTRODUCTION:

In our previous reports (1,2,3,4,5), 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, 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).

It was felt that an understanding of the mechanism of heavy metal adsorption, cationic and anionic, onto our modified-clays will be very helpful in establishing the potential for

Fig 1 Cu(II) Adsorption onto HCPA At pH 6.0:
Ionic Strength Effect

their use with actual industrial wastewaters. Therefore, we have carried out the following experiments to examine the effect of:

- Increasing concentration of 1:1 electrolytes on the adsorption of Cu(II) ions onto Hec-CBDA-PA, HCPA. From our earlier report (4), the optimum pH for this experiment was chosen to be 6.0.
- Spectral shifts that occur when Cu(II) ions complex with DT.
- The adsorption of ionogenic organic compound, β -naphthoic acid, 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 is expected to be a combination of anion exchange, hydrophobic partitioning and H-bond interaction.

In the following sections results from the above experiments are presented and discussed.

II. ADSORPTION OF Cu(II) onto HCPA: Effect of Ionic strength:

Adsorption experiments were carried out in a batch mode as has been described in our earlier reports. A 100 ppm stock solution of Cu(II) ions was made up and the modified-clay slurries were prepared by dispersing dry powders in buffer by sonication and vigorous mixing. The solution pH was maintained using buffer solutions which were 20 mM in ionic strength. For pH 6.0, an acetic acid/acetate buffer system was used. The adsorbent concentration was 1 mg/ml and the ionic strength was varied using stock NaCl solutions buffered to pH. 6.0. The initial Cu(II) concentration was varied between 1.0 - 30.0 mg/L. Positive controls (i.e. samples with no added adsorbent) were used to verify that Cu(II) ions were soluble in the buffered medium even at its highest initial

concentration. The results are shown in Fig.1. The data were fitted to a Langmuir type equation of the form:

$$q = \frac{q_0 \cdot K_a \cdot C}{1 + K_a \cdot C} \quad (1)$$

with q = adsorbed amount (mmoles Cu(II)/g adsorbent)
 q_0 = adsorbed amount at saturation (same units as q)
 K_a = Association constant (mM^{-1})
 and C = Cu(II) in solution (mM)

The values of association constants and the saturation capacities at each ionic strength are listed in Table 1. For comparison, similar data for Cu(II) adsorption onto Hec-CBDA-DT at pH 7.2 are also presented in Table 1.

Table 1: Adsorption of Cu(II) onto modified-hectorites: Ionic Strength Effect:

Ionic Strength (M)	Hec-CBDA-DT at pH 7.2		Hec-CBDA-PA at pH =6.0	
	Hec-CBDA-DT		Hec-CBDA-PA	
	q_0 (mmoles/g)	K_a (mM^{-1})	q_0 (mmoles/g)	K_a (mM^{-1})
0.02	0.34	30.3	0.25	88.5
0.05	0.40	13.4	0.19	33.7
0.1	--	--	0.18	37.7
0.2	0.66	2.56	0.13	34.7

The data presented in Table 1 reveal the following:

(1) The affinity of Cu(II) for COO^- groups on Hec-CBDA-PA is greater than it is for the amine groups on Hec-CBDA-DT. The driving force for adsorption in the former case consists of favorable coulombic and specific interactions between the negatively charged COO^- groups of PA and Cu(II) ions. In the case of Hec-CBDA-DT, the favorable free energy of adsorption due to the complexation reaction between Cu(II) ions and the amine groups on DT may have been offset by the electrostatic repulsion due to the residual positive charge on the surface resulting from a small number of unprotonated amine groups on the surface at pH 7.2. These charged amine groups are NOT expected to participate in the binding of Cu(II) ions.

(2) The affinity of Cu(II) adsorption decreases greatly with increasing ionic strength in the case of Hec-CBDA-DT. Since higher ionic strength is expected to provide greater electrostatic screening of the surface charge, it is not clear why the affinity declined by an order of magnitude. On the other hand, the decrease in the affinity in the case of Hec-

CBDA-PA is much smaller in magnitude. This is probably related to competition from the increased Na^+ ions in solution. Further work is in progress to clarify these issues.

(3) The increase in the saturation capacity for Cu(II) on Hec-CBDA-DT with increasing ionic strength may arise from interfacial precipitation of Cu ions due to a higher pH at the surface than in the bulk due to the positive charge of the amine groups on Hec-CBDA-DT. This is not the case with Hec-CBDA-PA and the saturation capacity decreases with increasing ionic strength as expected.

The above results show that a more definitive understanding of the mechanism of Cu(II) adsorption on Hec-CBDA-DT was needed and the following spectroscopic study was undertaken to determine the mechanism.

III. Complexation of Cu(II) by DT in Solution: A spectroscopic Study:

It was noticed that adsorption of Cu(II) onto Hec-CBDA-DT invariably imparted blue color to the adsorbent, which suggested the formation of a chelate between Cu(II) and DT. This was verified by the following Cu(II) complexation experiment in solution.

Aliquots of Cu(II) at a final concentration of 0.63 mM were reacted with increasing amounts of DT in pH 7.4 buffer. A parallel set of experiments was carried out in presence of 5 mM CBDA, which is 5 times the CMC of this cationic surfactant. A second batch of identical complexation tests were conducted at pH 3.3. At pH 7.4, the aqueous solution developed a blue color which became more intense with increasing amounts of DT. A spectral scan on a Varian DMS 200 UV-Vis spectrometer revealed a broad absorption band centered at 626 nm. The absorbance/turbidity of blank solutions containing all the components except Cu(II) ions was also measured at each pH. The results plotted in the form of absorbance ratio at 626 nm vs DT/ Cu(II) molar ratio in solution are shown in Fig. 2.

Fig. 2 Spectral Properties of Cu-DT Complex in Solution:
pH Effect

The results shown in Fig. 2 indicate that Cu(II) ions form charge-transfer type complexes with DT molecules in solution at pH 7.4 and NOT at pH 3.3. The absorbance ratio reaches a limiting value at a DT/Cu molar ratio of 3. Each DT molecule has two binding sites. Therefore, the observed DT/Cu(II) molar ratio would indicate a six coordinated Cu(II)-DT complex. However, many studies on "blue" copper proteins have established that the 626 nm band corresponds to a ligand-metal charge transfer band and that Cu(II) is in a flattened tetrahedral (four coordinated) configuration (7). Thus, we conclude that the stoichiometry of 3.0 observed in this study means that only a portion of DT ions are de-protonated. The actual geometry of the Cu(II)-DT complex is not known at this point.

The presence of CBDA, a cationic surfactant, lowers the intensity ratio, but not the stoichiometry of the Cu(II)-DT complexation. The lowering of the 626 nm band intensity is attributed to electrostatic repulsion from the cationic headgroups of CBDA towards cationic Cu(II) ions when the latter approach the surface of mixed CBDA-DT micelles.

The above spectral study verifies complex formation between Cu(II) and DT. It does not exclude the possibility of precipitation of Cu(II) ions at the interface due to a local pH much higher than the bulk. Further study is in progress to clarify these issues.

IV. Adsorption of Organic Acid onto MONT-DT: Surface Titration:

In one of our earlier reports (4), we reported on the development of MONT-DT and in our previous report (5), we demonstrated the anion exchange potential of MONT-DT by its adsorption of Cr(VI). We have undertaken a study of the adsorption of β -naphthoic acid onto MONT-DT to further elaborate upon the anion exchange capabilities of MONT-DT and to probe its surface charge characteristics as a function of pH. β -naphthoic acid is a common contaminant in many wastewaters and its properties are as follows:

Aqueous solubility of β -naphthoic acid:	70 ppm
pKa (8):	4.17

The procedure for the preparation of MONT-DT has been described in one of our earlier reports and the properties of MONT-DT are listed here for ready reference.

Properties of MONT-DT:

% Organic Carbon by weight:	41.6
% DT by weight:	50.4
mmoles of DT/g MONT-DT:	1.44

The origin of anion exchange in a DT molecule in solution and on the surface of MONT-DT is diagrammatically explained below in Fig. 3. The forces responsible for anion exchange are coulombic and non specific in nature and the exchange process results in an excess of negatively charged counterions near a positively charged surface. Thus, a deprotonated β -naphthoic acid can be expected to bind to MONT-DT, and if the adsorption of the organic acid is predominantly of the anion exchange type, then its surface excess as a function of pH will be a measure of the surface charge density of MONT-DT. β -naphthoic acid can also bind to MONT-DT surface through hydrophobic partitioning mechanism, but the extent of such adsorption is not expected to be high. Our results, as shown below, verify this hypothesis.

(A) Protonation-deprotonation of DT with pH

(B) pH Dependent exchange of anionic heavy metals and organic acids

Fig. 3 Anion Exchange mechanism for the adsorption of Cr(VI) and Organic Acids on MONT-DT

A stock solution of 50 ppm of β -naphthoic acid was prepared, from which the initial β -naphthoic acid (NA) concentration of 5 ppm was obtained by dilution with buffer. Using this initial concentration of NA, its adsorption onto MONT-DT was monitored at various pH ranging from 3.0 - 9.0. The amount of MONT-DT in these single-point adsorption isotherms was 0.05% W/V. NA concentration was assayed quantitatively using a fluorescence spectrometer. The excitation and the emission wavelengths were 287 and 360 nm respectively. Fluorescence intensity was measured in the ratio mode and a calibration curve in the 1 - 10 ppm NA range was used to determine NA concentration in isotherm samples.

The results of β -naphthoic acid adsorption onto MONT-DT as a function of pH are shown in Fig. 4. From the pKa data of NA, the percent of free acid concentration at each pH was computed and this is also included in Fig. 4. It can be seen that NA adsorption is maximal between pH 4.5 and 7.0, a pH range in which the % free acid goes to zero. This indicates the dominance of anion exchange mechanism. At higher pH (pH 9.0), adsorption is low mainly because of lower positive surface charge, further confirming the predominance of anion exchange as the adsorption mechanism. Finally, at pH 3.0, the positive surface charge is quite high, but the free acid concentration is ALSO high. Hence adsorption is not as strong.

Complete isotherms for the adsorption of NA onto MONT-DT were measured at pH 4.5, 7.0 and 9.0. The initial NA concentrations ranged from 2.0 - 20.0 ppm. The results are shown in Fig. 5.

The data presented in Fig. 5 reinforce our preliminary conclusions regarding the anion exchange mechanism for the adsorption of NA onto MONT-DT. The slopes of the linear isotherms are nearly the same at pH 4.5 and 7.0. At pH 9.0, the linear partition coefficient decreases by a factor 15. The residual adsorption at pH 9.0 is attributed to NA adsorbing onto hydrophobic patches on MONT-DT.

Fig. 4 Adsorption of Naphthoic Acid onto MONT-DT:
pH Effect

Fig. 5 Adsorption of Naphthoic Acid onto MONT-DT
Isotherms at three pH

The above studies on the adsorption clearly demonstrate that MONT-DT is mostly uncharged at pH 9.0, but is positively charged at pH 7.0. This explains why Cu(II) adsorption onto DT at pH 7.2 - 7.4 requires a DT/Cu(II) molar ratio of 3.0. In other words, only a portion of DT molecules are de-protonated at pH 7.0, and Cu(II) ions form complexes only with these uncharged surface amine groups.

V. REFERENCES:

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VI. Publications

- (1) On the Use of Modified-Clays for the Removal and Recovery of Heavy Metals From Wastewaters:
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 23 - 25, 1993.
Manuscript under review.

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