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A NOVEL, INTEGRATED TREATMENT SYSTEM FOR COAL WASTE WATERS:

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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. Adsorption of β -naphthoic acid (NA) onto hectorite-CBDA containing different amounts of adsorbed CBDA is pH dependent, stronger at pH 4.5 and much weaker at pH 8.6. Partitioning into the hydrophobic patches of hectorite-CBDA and binding as counter ion to CBDA bilayers appear to be the dominant mechanisms of adsorption of NA to hectorite-CBDA. Anionic Cr(VI) adsorbs very weakly to MONT-DT at pH 8.5 and this result verifies our earlier finding that the positive surface charge on MONT-DT decreases with increasing pH above pH 7.0. Potentiometric titrations of DT in water-isopropyl alcohol (IPA) binary solutions containing different volume fractions of IPA reveal that the pKa of DT is 7.6 ± 0.1 independent of IPA volume fraction. It is also shown that DT forms emulsions at pH lower than 4.0 and these emulsions tend to break up as pH is raised above 6.5. The formation of DT emulsions is reversible with respect to pH, but the process appears to be slow with a time constant of about 30 minutes.

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I. INTRODUCTION:

In our previous reports (1,2,3,4,5,6,7,8), 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 an earlier 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 (9). 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:	(<u>Hec-CBDA-DT</u> , HCDT, the diamine type)
(2)	Hectorite-CBDA-Palmitic Acid:	(<u>Hec-CBDA-PA</u> , HCPA, the carboxylic acid type)
(3)	Montmorillonite-Duomeen T:	(<u>MONT-DT</u> , the diamine type in which the functional moiety is directly attached to the clay surface)
(4)	Montmorillonite-CBDA-DT:	(<u>Mont-CBDA-DT</u> , 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 an intense absorption 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 respective 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 studied the adsorption of an ionogenic organic compound, β -naphthoic acid, (NA), as a probe of the surface charge density of MONT-DT and HCDT 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. It was shown that NA adsorbed to MONT-DT and HCDT strongly at pH 4.5 and 7.0, but weakly at pH 9.0 suggesting that the positive charge on the DT-modified clay surface is low at the latter pH (6, 7). Furthermore, Cr(VI) adsorption was also observed to be strong at pH 4.5, but very weak at pH 7.0 and 9.0 (7).

The above results showed, by inference, that DT-modified clay surfaces are only weakly charged (with a positive sign) at pH above 7.0. This inference was supported by the potentiometric titration of DT in aqueous solution with and without added Cu(II) ions to determine the basicity or the mean pKa of the diamine (8). The titrations were carried out in a binary solution of water-isopropyl alcohol (IPA) containing 5% IPA by volume. The mean pKa was observed to be 7.55. Furthermore, pH titrations and electrokinetic sonic amplitude (ESA) measurements on hec-CBDA-DT (HCDT) and MONT-DT were carried out to quantify surface charge of these clay complexes. The mean pKa was calculated to be 7.0 compared to 7.55 in solution.

- In the present quarterly report, we discuss the studies undertaken on the adsorption of β -naphthoic acid (NA) to hectorite-CBDA complexes in order to understand the mechanism of adsorption of NA to smectitic clays **containing only CBDA and no DT**.
- Details of adsorption of Cr(VI) on MONT-DT at pH 8.5 are presented and discussed.
- The variation of the pKa of DT as a function of IPA volume fraction and the emulsification of DT as a function of pH have been determined and these results are also presented and discussed.

II. Sorption of β -naphthoic acid (NA) to hectorite-CBDA Complexes:

Hectorite-CBDA complexes were prepared by reacting Na-hectorite with CBDA solution (4 mg/ml; 10.1 mM) in deionized water. CBDA amounts in the final complex corresponding to 30% (9.1 % by weight), 61.2 % (16.7 % by weight), 124 % (28.6 % by weight), and 184 % (37.4 % by weight) of the cation exchange capacity (CEC) of hectorite were prepared. The amount of adsorbed CBDA was taken as the difference between the initial and the final CBDA concentration in solution. Only a small amount of CBDA desorbed upon washing. The washed hectorite-CBDA complexes were re-suspended in aqueous solutions containing various amounts of NA at pH 4.5 and 8.6. The ionic strength was maintained at 20 mM. The results of NA uptake by hectorite-CBDA are shown in Figs 1 and 2.

Fig. 1 Adsorption of NA onto CBDA-Hectorite at pH 4.5

Fig. 2 Sorption of NA onto CBDA-Hectorite: pH 8.6

Fig. 3 Adsorption of Cr(VI) on MONT-DT at pH 8.5

The following observations can be made from the results shown in Figs 1 and 2. Since the pKa of NA is 4.17, the mole fraction of the unprotonated form of NA is 0.32 at pH 4.5

and 3.7×10^{-5} at pH 8.6. Furthermore, adsorption of NA at any pH can occur via following mechanisms:

- (1) H-bonding to surface OH groups of clays,
- (2) Sorption into hydrophobic patches on the surface formed by CBDA adsorption, and
- (3) Anion exchange as counterions on the edge sites of hectorite or on CBDA bilayers.

At pH 4.5, all the three modes of adsorption are possible, but the uptake of NA can be expected to be dominated by mechanisms (2) and (3). The data obtained were fitted to a site-specific, Langmuir type adsorption equation with following results.

Table 1: Langmuir Constants for the adsorption of NA on hectorite-CBDA:
pH =4.5

CBDA on hectorite-CBDA % CEC	K_a (mM^{-1})	q_0 (mmoles/g)	r^2 of the fit
0	--	--	No Adsorption
30.0	4.24	0.27	0.99
61.2	10.40	0.36	1.00
124.0	11.15	0.54	1.00
184.0	11.65	0.73	1.00

It is clear from the data shown in Table 1 that adsorption of NA is very weak to the base clay. Thus, the edge sites on the clay appear to be unimportant. Hydrophobic adsorption and counterion binding to CBDA bilayers are considered to be the dominant mechanisms. Our earlier results on NA adsorption onto MONT-DT and HCDT showed a much higher value of K_a , but a comparable value for q_0 . Thus, it would seem that anion exchange also contributes equally to NA sorption. On the other hand, NA sorption onto hectorite-CBDA is significantly weaker at pH 8.6. The linearity of the isotherms suggests that partitioning of NA into the hydrophobic patches of hectorite-CBDA surface is the only mechanism for NA uptake at this higher pH.

III Cr(VI) Adsorption onto MONT-DT at pH 8.5: Effect of Ionic Strength:

We have previously shown that adsorption of anionic Cr(VI) on MONT-DT is of the anion exchange type. Secondly, we have also established that the surface charge of MONT-DT becomes less positive at higher pH. Thus, Cr(VI) adsorption will be weaker as the pH is raised. This is verified by the results shown in Fig. 3. Sorption affinity and capacity are quite low at pH 8.5 and decrease with increasing ionic strength. The results with Tris ions are anomalous, and the possible explanations are: (1) Cr(VI) may have formed insoluble ion-pair complexes with cationic Tris or (2) the hydroxy ethyl tails of Tris may have bound to MONT-DT via hydrophobic attachment yielding positively-charged surface sites for Cr(VI) adsorption. Further work is in progress to confirm and seek a mechanistic explanation for these results. In conclusion, it may be pointed out that an anionic organic compound such as β -naphthoic acid and an inorganic anion such as Cr(VI) behave differently in response to changes in solution pH and surface charge characteristics.

Fig. 4 Titration of DT in Water-IPA and
Pentyl Diamine in Water:
Effect of IPA Concentration

Fig. 5 pH Dependent Emulsification of DT

Fig. 6 pH dependent Emulsification of DT:
Effect of IPA Volume Fraction

IV. Potentiometric Titration of DT: Effect of IPA Concentration:

From our previous studies on the pH titration of the diamine, DT, a mean pKa of 7.55 was obtained for DT in a water-IPA binary solution containing 5% by volume of IPA. In this report, we have extended the study to examine the effect of IPA volume fraction on the mean pKa of DT. By extrapolating the measured pKa values to zero volume fraction of IPA, an apparent pKa of DT in aqueous solution can be obtained. This latter value of pKa is more relevant since all of our previous work on the adsorption/desorption of heavy metal ions were undertaken in aqueous solutions at constant ionic strength, but with no IPA.

DT was titrated with 2 M HCl at various volume fractions of IPA and the results are shown in Fig. 4. The three lower curves (obtained at different volume fractions of IPA) in Fig. 4 are co-incident indicating that the observed pKas are independent of IPA volume fraction. A quantitative measure of this was obtained by fitting each one of the curves to a 4th degree polynomial and solving the resulting equation for the inflection point. The corresponding mean pKa was found to be 7.6 ± 0.1 .

A further verification of the procedure was obtained by titrating a homogeneous diamine (DYTEK) obtained from Dupont Chemicals. The properties of DYTEK are listed below in Table 2.

Table 2: Properties of DYTEK diamine (DDA):

Property	Description
Name:	1,5-pentanediamine, 2-methyl
Formula:	$\text{NH}_2\text{CH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_3\text{NH}_2$
MW:	116.2 g/mole
Purity:	99%
Form:	Liquid at Room Temperature
Water Solubility:	Miscible
Mean pKa:	10.56
pKa 1:	11.1
pKa 2:	10.02

The upper titration curve for DYTEK (Fig. 4) shows a distinctly different behavior compared to the lower curves corresponding to DT titration. The end point is much sharper, and, secondly, the mean pKa was found to be **10.5** using a procedure identical to the one used for DT. The mean pKa value obtained in this study is quite close the literature value (reported in Table 2) and thus provides verification for our procedure.

V. pH dependent emulsification of DT:

Our previous study has shown that DT attached to MONT-DT and HCDT is stable with respect to desorption from the surface due to the extreme insolubility of DT in water. One of the unanswered questions is whether DT's aqueous solubility will be affected by solution pH. Specifically, at lower pH (< 5.0) DT may become more water-soluble due to positive surface charge on DT molecules and this may facilitate a favorable ion-dipole interaction between DT and water molecules. Secondly, the solubility of DT in aqueous media may also modified by the presence of IPA.

DT was titrated with 2 M HCl and, during titration, the turbidity of the solution was monitored after each addition at 500 nm. Low turbidity would be an indication of the existence in solution of a single phase or a single phase along with a pseudo micellar

phase. Increasing turbidity, on the other hand, will result from the emulsification of DT molecules with the possibility of further phase separation due to settling of over-grown emulsion particles.

The results of the potentiometric titration are shown in Figs 5 and 6. The pH -turbidity plot obtained in presence of 0.99 % IPA by volume is shown in Fig. 5 and has three partially overlapping regions:

Region I: In the pH range of 10.0- 6.5, the turbidity is low because DT is well dispersed but not dissolved in water-IPA solution. The droplet size of the emulsion is quite low, accounting for low turbidity.

Region II: In the pH range 6.5 - 4.0, the turbidity is almost zero indicating a transition to an emulsion containing even smaller droplets or a microemulsion pseudo phase.

Region III: Below pH 4.0, the turbidity increases rapidly as the emulsion droplets grow in size. At this pH, DT is fully protonated, but appears to be less stable, colloiddally speaking. This is surprising because the ionic strength is close to zero.

The formation of unstable emulsion at pH less than 4.0 is further verified by the hysteresis in the turbidity-pH plot when DT is back-titrated with 1 M NaOH. As more NaOH is added, the turbidity "lags" behind pH due to a slow break up of emulsion droplets in response to higher solution pH. However, the titration is "reversible" as evidenced by the fact that turbidity returns to its original value after a 30 minute waiting period.

The effect of increasing concentrations of IPA on the stability of DT emulsions is further examined in Fig. 6. As the volume fraction of IPA is increased formation of DT emulsion at the lower pH is delayed. This is due to the fact that the presence of IPA lowers the tendency of DT to aggregate. However, DT molecules do eventually aggregate to form turbid emulsions.

Further work is in progress to clarify the afore-mentioned issues regarding the emulsion stability of DT in aqueous media.

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