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A NOVEL, INTEGRATED TREATMENT SYSTEM FOR COAL
WASTE WATERS:

QUARTERLY REPORT:

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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. A specific goal of the study is to remove and recover cationic and anionic heavy metals from aqueous solutions and coal conversion waste waters using modified-clay adsorbents developed in this study. To this end, a multi-step adsorption/desorption process has been carried out with hectorite-CBDA-DT (HCDT) as the adsorbent and Cr(VI) as the adsorbate. Adsorption was carried out at pH 4.0 in 0.02 M buffer, while desorption was effected at the same pH and in the same buffer with either 0.5 M NaCl or 0.02 M Na₂SO₄ as the desorbates. Multi-step involves cycling the same adsorbent through these two sets of operating conditions with a washing step after each adsorption/desorption sequence.

Our results indicate that, during the first two cycles, the potency of the adsorbent remains unchanged, but it diminishes after the third and the fourth cycles. The total decrease in potency is, however, only 15% even after 4 cycles of adsorption/desorption. Addition of 20% isopropyl alcohol (IPA) to the reaction medium, however, diminishes the potency even more after 4 cycles of adsorption and desorption. Both the desorbates yielded identical results, and the overall mass balance on Cr(VI) was between 95 and 102%.

Continuous leaching experiments on HCDT revealed that DT bound to HCDT is mobilized to the extent of only 10% after 44 hrs in aqueous medium while in 20% IPA-water mixtures the extent of dissolution of DT from the surface is close to 16%. Thus, the loss of potency of HCDT is attributed partly to the loss of DT from the surface and partly to the incomplete washing of the adsorbent between each adsorption/desorption step.

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I INTRODUCTION:

In our previous reports (1,2,3,4,5,6,7,8,10,11), 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 is first treated upto a monolayer (or the charge equivalence point) with a quaternary ammonium surfactant CBDA, a treatment that imparts 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 yields a mixed bilayer on the clay surface and such clays have been 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), is 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 are 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 de ionized 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 also 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. It was also observed that the pKa of DT is 7.6 ± 0.1 independent of IPA concentration (10). Further analysis of the adsorption of β -naphthoic acid (NA) to CBDA-hectorite containing no DT confirmed our earlier results that NA binds to surfactant-modified clay surfaces through a combination of hydrophobic and counter ion binding mechanisms (10).

A multi-step adsorption/desorption procedure has been used to evaluate the extent to which the adsorbents can be re-used without a significant loss in sorption affinity or capacity for heavy metals. In the last report, we discussed a five-step adsorption-desorption process using pH shift to effect adsorption or desorption of the metal ions from sorbent surface. It was shown that we were successful in the case of Cu(II), but not so effective in the case of Cr(VI). In the former case, less than 15% loss of efficiency was observed, but in the latter case the adsorbent appeared to have lost about 40% of its potency through a similar five-step cycle. Furthermore, the average mass balance on Cu(II) through each adsorption/desorption cycle was 95% compared to an average of only 75% in the case of Cr(VI). Since Cr(VI) has been shown to adsorb mainly as counterions, its binding is expected to be sensitive to the pH and the ionic strength of the medium. Presence of residual positive charge on the adsorbent at the higher pH (10-11) may have resulted in incomplete desorption of Cr(VI) at the higher pH and this may have led to an apparent loss in sorption efficiency. This may also explain the poor mass balance observed in this case. Cu(II) adsorption, on the other hand, has been shown to occur through chelate formation on the surface and is only pH sensitive.

In the present quarterly report, we discuss the studies undertaken:

- To examine the feasibility of multi-step adsorption/desorption of Cr(VI) onto HCDT at a constant pH (pH = 4.0). The ionic strength of the medium was varied to bring about desorption. 0.5 M NaCl or 0.02 M Na₂SO₄ were used as desorbates.
- To quantify the effect of addition of 20% (V/V) isopropyl alcohol (IPA) to the medium during the multi-step adsorption/desorption of Cu(II) and Cr(VI) from HCDT. The primary purpose of addition of 20% IPA is to simulate the presence of water-miscible organic solvents in a typical waste water. Furthermore, the surface-bound DT, which has been shown to be stable due to its insolubility in aqueous solutions may become mobilized due to the presence of IPA in the medium. Thus, a better understanding of the stability of adsorbed DT under different conditions is the expected result from such a study. We have also followed the kinetics of leaching of DT from the surface in deionized water and in 20% (V/V) IPA-water binary solutions.

II. Multi-Step Adsorption and Desorption of Cr(VI) onto HCDT at constant pH: Effect of Ionic Strength.

Multi-step adsorption and desorption of Cr(VI) onto HCDT was carried out as described in our previous report. The following table is a summary of the experimental conditions used.

Table 1: Experimental Conditions for Multi-step Cr(VI) adsorption/desorption:

System Variable	Operating Conditions
Adsorbent and its Mass	HCDT; 20 mg Total
Volume of Batch Reactor	10 ml
Adsorption/desorption pH	4.0
Adsorption Medium	0.02 M Na Acetate/Acetic Acid
Desorbates	0.5 M NaCl or 0.02 M Na ₂ SO ₄ in Adsorption medium
Initial Cr(VI) Concentration	20 ppm (0.38 mM)
Adsorption/desorption Time	2 hrs each
Method of analysis	AAS
Method of Phase Separation	Centrifugation
Temperature	22 ± 1°C

The experimental sequence for a single adsorption/desorption step was to adsorb Cr(VI) onto HCDT, remove the entire supernatant after centrifugation and initiate desorption by adding 10 ml of desorption solution. After desorption, the entire supernatant solution was removed following phase separation by centrifugation. The sedimented adsorbent was washed and re-equilibrated twice in 10 ml of adsorption medium, following which the entire cycle was repeated 3 times. The concentration of Cr(VI) in the adsorption and desorption supernatants was assayed by AAS. Mass balance for each cycle was deemed to be the sum of Cr(VI) concentrations in the two supernatants divided by the initial Cr(VI) concentration. As mentioned before, desorption of adsorbed Cr(VI) was attempted using either 0.5 M NaCl or 0.02 M Na₂SO₄.

The results are shown in Figs 1A, 1B, 2A, and 2B.

Fig. 1A Multi-step Adsorption/Desorption of Cr(VI) from HCDT at pH 4.0

Fig. 2A Multi-Step Adsorption/Desorption of Cr(VI) from HCDT at pH 4.0

Fig. 1B Multi-Step Cr(VI) adsorption/Desorption: Mass balance

Fig. 2B Multi-Step Adsorption/Desorption of Cr(VI) from HCDT: Mass Balance

Fig. 3A Multi-step Adsorption/Desorption of Cu(II) from HCDT: Effect of IPA (20% V/V)

Fig. 4A Leaching of adsorbed DT by H_2O and 20% IPA- H_2O

Fig. 3B Multi-step Adsorption/Desorption of Cr(VI) from HCDT: Effect of 20% IPA (V/V)

Fig. 4B Leaching of DT from modified-clays: Mass Balance

It can be seen from Fig. 1A that the first two cycles of adsorption/desorption produced very little change. The mass balances for these two cycles range between 95 and 102%. However, the extent of Cr(VI) removal during the adsorption part of the cycle decreases between cycles 3 and 4. The mass balances are, however, still close to 100%.

There are three possible explanations for the deterioration in the performance of HCDT with increasing adsorption/desorption steps.

- (1) DT, the active component in the uptake of Cr(VI), is slowly being leached from the surface of HCDT.
- (2) The two washing steps between each cycle are insufficient to return the adsorption medium to its original ionic strength of 0.02 M.
- (3) There is a continual loss of the adsorbent, HCDT, during the centrifugation and the washing operations involved in each cycle.

The relative importances of these possibilities are discussed in the next two sections.

The data displayed in Figs 2A and 2B reveal that 0.02 M Na_2SO_4 is as effective as 0.5 M NaCl in promoting desorption of adsorbed Cr(VI). The mass balance, except for the second cycle, is around 100%. The potency of HCDT (just as in the case of 0.5 M NaCl) appears to diminish with increasing adsorption/desorption cycles.

The combined results of all the four figures demonstrate that **a shift in the ionic strength of the medium rather than its pH is a better method to recycle the modified-clay adsorbent, HCDT, through multiple Cr(VI) adsorption and desorption steps.** This conclusion is in agreement with our earlier findings that Cr(VI) adsorption onto HCDT is mostly, but not totally, electrostatic in nature. A specific component to the free energy of adsorption of Cr(VI) is indicated by the fact the background electrolyte concentration in the adsorption medium at the lower pH is 50 times higher than the initial Cr(VI) concentration.

III. Multi-step Adsorption/Desorption in Presence of 20% IPA(V/V):

Multi-step adsorption and desorption of Cu(II) by pH shift and that of Cr(VI) by change in ionic strength at constant pH was carried out in presence of 20% IPA (V/V). The sequence of operation during each cycle was (a) adsorption, (b) desorption, and (c) washing, followed by the next cycle. IPA was added to the buffer medium only during steps (a) and (c). The results are shown in Fig. 3A for Cu(II) and Fig. 3B for Cr(VI).

The potency of HCDT is unchanged through three cycles in the case of Cu(II) and diminishes significantly during the fourth cycle. A more gradual loss of effectiveness is observed with Cr(VI) (Fig. 3B). The mass balance in all cases ranges between 88 and 108%.

It is apparent that the addition of 20% IPA, a good solvent for DT, to the buffer medium may have enhanced the mobilization of DT from the surface of HCDT and this may be the cause of diminished effectiveness of HCDT upon repeated use. In order to verify this possibility, separate leaching experiments were carried out.

IV. Leaching of DT from DT-modified clays:

Batch leaching experiments were conducted in 20 ml reactors with continuous mixing. Each reactor contained a total of 20 mg HCDT or MONT-DT and the dispersion medium

was either de ionized water or 20% IPA-de ionized water mixture. The suspension was centrifuged at different time intervals and 3 ml of the supernatant were removed and replaced by an equal volume of de ionized water or IPA-water mixture and the leaching experiment was continued.

The above aliquot of the supernatant was filtered through a 0.22 μm filter and the molar concentration of NH_2 group in the supernatant (which is stoichiometrically equivalent to the molar concentration of DT in solution) was determined by the Ninhydrin method. The Ninhydrin method is widely used to assay NH_2 groups (12) and the commercially-available Ninhydrin reagent was calibrated using ϵ -amino caproic acid as a standard. The following correlation between absorbance at 570 nm, (A_{570}), and μmoles of NH_2 groups/ml was used.

$$\text{Conc. } (\mu\text{moles } \text{NH}_2/\text{ml}) = -0.0841 + 0.463 * (A_{570})$$

After 44 hours of leaching, a sample of the entire suspension was also assayed by the Ninhydrin method to determine the surface concentration of NH_2 groups on HCDT or MONT-DT. As a check on the reliability of the Ninhydrin method in the case of immobilized NH_2 groups, lysine covalently-bound to solid agarose was used as a standard. The Ninhydrin method used by us yielded a **95.5 % correlation** between our values and the literature values for lysine-agarose.

The results of leaching experiments are shown in Figs 4A and 4B. The total number of μmoles of DT was obtained by summing the total number of μmoles of DT in each of the supernatants together with the μmoles of DT bound to the surface at the end of 44 hours. As shown in Fig. 4A, less than **10% of DT** that was initially present either on HCDT or MONT-DT is leached by de ionized water in 44 hours. On the other hand, 20% IPA-water mixture mobilizes about **16% of DT** from the adsorbents. It is interesting to note that both HCDT and MONT-DT show similar stability to leaching (Fig. 4B) even though they are prepared by different methods. This indicates that the mass transfer characteristics of the two adsorbents are nearly the same. This suggests that the DT molecules that are released during the initial stages of leaching are loosely bound to the surface, most likely on the external surface of the clays.

In the case of Cu(II) , the loss in adsorption potency with repeated use (a maximum of 15%) can be accounted for by the extent of leaching of DT from the surface both in aqueous solutions and in 20% IPA-water mixtures. With Cr(VI) , the loss of potency (as high as 40%) has to be attributed to all the three mechanisms listed on page 6.

It should be noted that the above leaching experiments were carried out with vigorous mixing at ambient temperature. In actual applications of modified-clays, the degree of mixing will be significantly less severe, thus the results reported here represent the **worst case scenario**. By the same token, a higher operating temperature may result in a higher rate of leaching of DT both in aqueous solutions and in IPA-water mixtures. Some of these issues will be considered in subsequent reporting periods.

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