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A NOVEL, INTEGRATED TREATMENT SYSTEM FOR COAL
WASTE WATERS:
QUARTERLY REPORT:
FOR THE PERIOD December 2, 1993 - March 1, 1994.

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Submitted to:

Pittsburgh Energy Technology Center
U. S. Department of Energy
Pittsburgh, PA.

ABSTRACT:

One of the specific aims of the study has been to remove and recover cationic and anionic heavy metals from aqueous solutions using modified-clay adsorbents developed in this study. To this end, hectorite-CBDA-DT (HCDT), one of the adsorbents we have so far prepared, has been used in a multi-step adsorption/desorption process. Briefly, the multi-step adsorption/desorption process involves initially contacting the adsorbent with a solution of heavy metal ion (Cu(II) or Cr(VI)) at a pH which corresponds to maximal adsorption of the respective metal ion (7.4 or 8.8 for Cu(II) and 3.5 - 4.0 for Cr(VI)). Desorption of adsorbed metal ion is effected by adjusting the solution pH to a value at which the respective metal ion is optimally desorbed (3.0 for Cu(II) and 10.0 for Cr(VI)). Multi-step involves cycling the same adsorbent through the two pH values repeatedly. Our results indicate that, for Cu(II) ions, HCDT can be used at least 5 times and the loss of adsorption (removal) and desorption (recovery) efficiency is only 15% of the initial value. Further, the overall mass balance of the Cu(II) system is 95%. However, with Cr(VI), the same adsorbent loses more than 40% of its potency after 4 cycles. Further, the overall mass balance averages to only 75% in the case of Cr(VI) removal and recovery. It is believed that differences in the operational performance in the two cases can be attributed to different adsorption mechanisms: Surface chelate formation (dependent only on local pH) and counter ion binding (responsive to local pH and ionic strength) respectively in the case of Cu(II) and Cr(VI).

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Our results indicate that, for Cu(II) ions, HCDT can be used at least 5 times and the loss of adsorption (removal) and desorption (recovery) efficiency is only 15% of the initial value. Further, the overall mass balance of the Cu(II) system is 95%. However, with Cr(VI), the same adsorbent loses more than 40% of its potency after 4 cycles. Further, the overall mass balance averages to only 75% in the case of Cr(VI) removal and recovery. It is believed that differences in the operational performance in the two cases can be attributed to different adsorption mechanisms: Surface chelate formation (dependent only on local pH) and counter ion binding (responsive to local pH and ionic strength) respectively in the case of Cu(II) and Cr(VI).

I INTRODUCTION:

In our previous reports (1,2,3,4,5,6,7,8,10), 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 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 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 function of pH to probe the surface charge density of MONT-DT and HCDT. 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).

- In the present quarterly report, we discuss the studies undertaken to examine the feasibility of multi-step adsorption of Cu(II) and Cr(VI) onto HCDT.

II. Multi-Step Adsorption and Desorption of Cu(II) and Cr(VI) onto HCDT:

Application of surfactant-modified clays developed so far in this study to the removal and recovery of heavy metals from aqueous solutions requires that the adsorbent be used and re-used many times without any loss of sorption affinity or capacity. Such re-use will greatly enhance the cost effectiveness of modified-clay adsorbents in field applications.

The following batch adsorption/desorption scheme was devised to explore the feasibility of multi-step adsorption and desorption of Cu(II) and Cr(VI) onto HCDT.

A 5 mg/ml suspension of HCDT was suspended and sonicated in a pH 7.4 aqueous solution containing 20 mM NaCl. pH was adjusted using HCl and NaOH solutions. Suspensions of HCDT (10 ml total volume containing 20 mg HCDT) were mixed with an initial Cu(II) concentration of 20 ppm (0.32 mM). After 2 hrs of adsorption, clay was separated by centrifugation and the entire supernatant solution was carefully removed for Cu(II) assay by atomic absorbance spectroscopy (AAS). Desorption of adsorbed Cu(II) was carried out by contacting the sedimented HCDT with a pH 3.0 solution at the same

Fig. 1 Multi-step Adsorption and Desorption
of Cu(II) from HCDT:

Adsorption pH 7.4; Desorption pH 3.0

Fig. 2 Multi-Step Adsorption and Desorption
of Cu(II) From HCDT:

Adsorption pH 8.8; Desorption pH 3.0

Fig. 3 Multi-step Adsorption and Desorption
of Cu (II) on HCDT:
Mass Balance on Cu(II)

Fig. 4 Multi-Step Adsorption and Desorption
of Cr(VI) on HCDT:
Adsorption pH 3.5 - 4.3; Desorption pH 8.5 - 10.0

ionic strength. Desorption was allowed to proceed for 2 hours and the solid/liquid separation was effected once more by centrifugation. The desorption supernatant was withdrawn and analyzed for Cu(II) by AAS.

The above step of adsorption and desorption was repeated by re-suspending the sedimented HCDT in fresh pH 7.4 solution and re-adjusting the pH with very small volumes of concentrated HCl or NaOH, if necessary. A fresh aliquot of Cu(II) solution was added and the process of adsorption and desorption continued.

A second set of multi-step adsorption/desorption of Cu(II) from HCDT was carried out by cycling solution pH between 8.8 and 3.0. In this case, pH at the higher pH was maintained using bicarbonate/carbonate buffer system at an ionic strength of 0.02 M. Even then, it was observed minor pH adjustments with concentrated HCl or NaOH had to be made.

Similar adsorption and desorption experiments were performed on Cr(VI) uptake and release from HCDT. In this case, the adsorption pH was between 3.5 - 4.4 and desorption was carried out at pH 10.0.

The results are shown in Figs 1 - 4. As shown in Fig. 1, during the first adsorption step at pH 7.4, Cu(II) ions adsorb very strongly to HCDT and more than 95% of the Cu(II) initially added is bound to HCDT. Further, it can be seen that the bound Cu(II) ions are quantitatively desorbed during the first desorption step. During subsequent adsorption desorption steps (steps 2 - 5, Fig. 1) the efficiency of Cu(II) uptake and removal is lowered by 15%. **However, the fractional removal of Cu(II) ions from solution at pH 7.4 (85 - 87% of the initial amount) and their subsequent quantitative recovery from the adsorbent surface at the lower pH become invariant with the extent of re-use of the same adsorbent.** Control experiments with Cu(II) ions at the identical initial concentration (20 ppm ; 0.32 mM) show no loss of Cu(II) ions from solution by precipitation or nonspecific adsorption.

Carrying out the multi-step adsorption/desorption experiment at a higher adsorption pH of 8.8 produces similar results, as shown in Fig 2. The extent of Cu(II) adsorption averages around 87% of initial Cu(II) concentration and the recovery of the adsorbed Cu(L) is quantitative at the lower pH.

The overall mass balance for the multi-step experiment is depicted in Fig. 3. It can be seen that mass balance ranges from 90 - 102 % with a mean mass balance of 95%. The data presented in Figs 1 - 3, taken together, show that HCDT can be used at least five times to remove and recover Cu(II) ions from aqueous solutions.

On the other hand, similar multi-step experiments with Cr(VI) are not as promising. First of all, the extent of Cr(VI) removal at the lower pH decreases with every re-adsorption step. At the fourth step, Cr(VI) removal efficiency during the adsorption step decreases from 99% at the first step to about 60%. Further, the mass balance (shown under each data point) is as low as 65% and is less than 90% in all cases.

The observed differences in the behavior between Cu(II) and Cr(VI) can be explained as follows: Cu(II) adsorption is a direct result of surface chelate formation, sensitive only to local pH. On the other hand, Cr(VI) binding to the surface is of the counter ion type and is modified by surface charge (dependent upon local pH) and the solution ionic strength. HCDT has residual positive charge even at pH 10.0, hence Cr(VI) removal may not be quantitative. The continual build up of Cr(VI) on the surface due to repeated use may also explain why the over all mass balance is poor for Cr(VI).

Further work is in progress to clarify the issues raised by this study.

III. Conclusions.

It is clear that HCDT, one of the modified-clay adsorbents prepared under the present grant, can be used many times over to remove and recover cationic heavy metals such as Cu(II). With anionic heavy metals such as Cr(VI), multiple uses of the adsorbent are not as effective.

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