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NOVEL SORBENTS FOR COAL CONVERSION WASTEWATER TREATMENT:

QUARTERLY REPORT

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ABSTRACT:

In this report, we describe the results from a study undertaken to scale-up the clay modification procedure. Hitherto, adsorption of toxic organics found in coal conversion wastewater onto modified clays was carried out in a batch mode utilizing small amounts of the adsorbents. A realistic evaluation of the potential of modified clays as adsorbents under field conditions necessitates the development of continuous wastewater treatment schemes requiring larger amounts of the adsorbents. Hence a need arose for the scale-up of clay modification procedure. Three types of surfactant-modified clays, namely, cetylpyridinium-emathlite (CPC-EMAT), cetylpyridinium-montmorillonite (CPC-MONT), and cetylpyridinium hydroxy aluminum montmorillonite (CPC-HYDAL-MONT) were prepared by a one-step method discussed in our previous report (ref.8). Emathlite (EMAT) is a commercial mixture of clay minerals, whereas montmorillonite is a well-characterized, research-grade smectite. Comparison of the amounts of adsorbed surfactant prepared by this method and an earlier method showed that the two procedures yielded identical results.

Using 3,5,-dichlorophenol (DCP) as a toxic organic, packed bed adsorption experiments were carried out with CPC-EMAT and CPC-HYDAL-MONT as adsorbents. A step input of the adsorbate at different flow rates was used and the dynamic adsorption capacity of the adsorbents for the toxic organic (i.e. DCP) was determined.

I. INTRODUCTION:

In our earlier reports (1,2,3,4,5,6,7,8), we demonstrated the effectiveness of modified clay sorbents in removing benzo(a)pyrene, (B(a)P), pentachlorophenol (PCP), and fluorene (FLE) from aqueous solutions. The key accomplishment of our research efforts to date has been the DEVELOPMENT of modified clay adsorbents, a typical example being CPC-HYDAL-MONT, which match or exceed the performance of granulated activated carbon (GAC) for the target, coal wastewater pollutants listed above.

Secondly, packed bed adsorption experiments with modified clays revealed a strong binding of B(a)P to modified clay columns with no indication of a breakthrough of B(a)P in effluent stream. Furthermore, experiments were carried out to establish the stability of modified clay sorbents and to verify the postulated orientation of surface organic carbon; i. e. the hydrocarbon tails and the cationic head groups of the surfactant molecules were pointing towards the surface and the dispersion medium respectively.

A thermodynamic analysis of the formation and the stability of IOCs was presented, which indicated that cohesive energy arising from lateral interactions between C_{16} chains of CPC ion can more than compensate for the unfavorable interaction between the positively charged surface and the cationic head group of the surfactant. In other words, it was recognized that a balance between electrostatic and chemical (hydrophobic) forces was the key to the success of our IOCs. A further understanding of this force balance was obtained from experiments carried out with positively charged, and highly dispersed alumina particles. It was shown that lowering of the surface positive charge of by complexation with phosphates or citrates was essential to facilitate the adsorption of cationic surfactant,CPC, on alumina surfaces. Adsorption of PCP onto surfactant-modified kaolinite (i. e. CPC-Kaolinites) was carried out to establish the role of the surface orientation of the adsorbed surfactant on the sorption potential of the sorbent.

Further, a study to optimize the amount of surface organic carbon was undertaken, and it was shown that optimal adsorption of benzo(a)pyrene, (B(a)P), could be effected with a surfactant weight percent of 5.5%. On the other hand, a strong adsorption of pentachlorophenol (PCP) was found to require at least 14% by weight of surface organic carbon. Thus, it was shown that modified clay adsorbents can be gainfully modulated to adsorb different types of pollutants from coal conversion wastewaters. Adsorption studies using the actual coal conversion wastewaters obtained from The Coal Liquefaction facility at Wilsonville, Alabama were also undertaken. Both PCP and B(a)P dissolved in coal conversion wastewaters were shown to bind strongly to our modified clays. Secondly, in coal conversion wastewaters, our modified clays and activated carbon were observed to function equally effectively in the case of B(a)P. In the case of PCP, modified clays performed better than activated carbon.

A major objective of our research, namely to extend our clay modification procedure to commercially available clays was also achieved. A typical commercial clay known as emathlite (EMAT), costing only $ 0.058/lb, was chosen and an one-step modification procedure (in which EMAT was treated directly with CPC to form CPC-EMAT) was shown to be as effective as the two-step process adopted for the preparation of CPC-HYDAL-MONT. Thus, a major step towards the commercial viability of modified clays as adsorbents was taken. From the adsorption of PCP and FLE, it was shown that CPC-EMAT and CPC-HYDAL-MONT were functionally equivalent.

Studies were also undertaken to explore the structural equivalence of CPC-EMAT and CPC-HYDAL-MONT. Specifically, the long term stability of CPC-EMAT with regard to desorption of the adsorbed surfactant was considered. Electrokinetic measurements as well as flocculation tests were carried out to discern the surface orientation of the adsorbed surfactant. These studies revealed the structural equivalence of CPC-EMAT and CPC-HYDAL-MONT.

In the final year of the present project, it was deemed necessary to carry out large scale packed bed adsorption experiments to test the dynamics of the sorption process. Previous batch adsorption experiments involved the use of very small amounts of the sorbent (5 - 10 mg per test) and were carried out for 24 hrs to allow the process to reach an equilibrium. However, it was felt that a realistic assessment of the potential of modified clay sorbents under actual field conditions can be obtained only from unsteady state sorption experiments using a packed bed adsorber and much larger amounts of the adsorbent (in gram amounts). This required an optimal scale-up procedure to prepare larger amounts of modified clays necessary for such a venture.

3,5 - dichlorophenol was chosen as the target adsorbate because of its structural similarity to the dihydroxy phenolics usually found in coal conversion wastewaters. Secondly, because of its its high aqueous solubility, (4.5 mg/ml (9)), a high influent concentration could be used so that both the breakthrough and the end point of adsorption could be reached in a reasonable amount of time. The breakthrough and the end point of adsorption are defined respectively as the points in the effluent profile at which the effluent concentration becomes nonzero and equal to the influent concentration.

II. SCALE-UP OF CLAY MODIFICATION PROCEDURE:

The steps involved in the preparation of modified clay were similar to the ones used earlier except that extensive washing procedure was carried out at the end of the modification procedure. A typical flow sheet for the preparation of CPC-HYDAL-MONT is as follows:

(1) Disperse Na-MONT (SWY-1) in deionized water
(2) Treat with 4 mM NaCl to ensure conversion of the clay to the Na form
(3) Separate excess NaCl by centrifugation and decant the supernatant.
(4) Re-suspend the clay in hydroxy aluminum solution to exchange Na for hydroxy aluminum.
(5) Separate excess hydroxy aluminum by centrifugation and decant the supernatant.
(6) Re-suspend the HYDAL-MONT in a mixture of CPC and HYDAL solution.
(7) Wash extensively to remove excess CPC and HYDAL.
(8) Dry at 110^{0}C and grind to a fine powder.

CPC-MONT and CPC-EMAT were prepared by mixing Na-MONT and EMAT directly with the required amount of CPC. The modified clays were then extensively washed, dried and ground prior to use.

The above procedures were used routinely to prepare 50 - 100 gram batches of the modified clays with yields close to 100%.

III. CHARACTERIZATION OF MODIFIED CLAYS:

In order to verify that the scale-up procedure yielded modified clays qualitatively and functionally similar to the ones obtained earlier in this project, the surface concentration of the surfactant was determined by pyrolysis of modified clay samples at 580^{0}C. Since different clay samples may imbibe varying levels of moisture due to storage at room temperature, all the samples were heated initially at 110^{0}C to obtain the " dry " weight before the pyrolysis step to determine the surfactant concentration. The final surfactant concentration is thus related to the "dry" weight of the modified clays. A correction was applied for the fact that even unmodified clay loses weight upon pyrolysis due to dehydroxylation of surface hydroxyl groups. Thus, Na-MONT, EMAT and HYDAL-MONT were also heat-treated similarly, and their respective weight losses were taken into account when determining the actual amount of the adsorbed surfactant in each case. The results are summarized in Table 1.

TABLE 1

CLAY TYPE	% WEIGHT LOSS[1] 110^{0}C	580^{0}C	WEIGHT PERCENT SURFACTANT [2]
Emathlite (EMAT)	4.3	3.4	-------
CPC-EMAT	26.9	16.8	13.4 (13.0)[3]
Na-MONT	4.9	2.5	-------
CPC-MONT	1.6	23.7	22.1 (23.0)
HYDAL-MONT	1.4	11.2	-------
CPC-HYDAL-MONT	2.0	27.9	16.7 (17.0)

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1 The percent weight loss is the mean of measurements in triplicate. The mean standard error was less than 4%. The reported weight losses at 110^{0}C and 580^{0}C are based on the weights at room temperature and the weight at 110^{0}C respectively.

2 The weight percent surfactant on a given surfactant-modified clay was calculated to be the difference between observed weight losses of the organo-clay and the unmodified clay.

3 The values given in parentheses refer to the highest surfactant weight percent that had been previously observed for the same adsorbent.

The following observations can be made from the results shown in Table 1.

(1) The surface organic carbon content obtained by this new procedure is nearly indistinguishable from our earlier results obtained on much smaller batches of clays. Thus, the scale-up procedure may be deemed to be successful.

(2) CPC-EMAT appears to have imbibed high levels of moisture during storage at room temperature. Since EMAT by itself shows only moderate amounts of weight loss (4.3% when compared to 26.9% for CPC-EMAT), this imbibition of water molecules at room temperature can not be attributed to impurities either in CPC or EMAT.This phenomenon is being investigated.

(3) Extensive washing of the surfactant-modified clays has not resulted in any significant levels of surfactant desorption. Thus, the apparent " irreversibility " of the surfactant adsorption reported earlier by us appears confirmed even with scale-up procedures.

(4) The significant weight loss observed with HYDAL-MONT arose from the dehydroxylation of adsorbed hydroxy aluminum, both in the interlayer space of montmorillonite as well as on the external surfaces of the clay. Such a phenomenon has been observed by earlier workers (10, 11).

IV. PACKED BED ADSORPTION OF DCP BY MODIFIED CLAYS:

The modified clay samples prepared and characterized as described above were used in an all-glass column to quantify the unsteady state adsorption of DCP. DCP was chosen because of its high aqueous solubility, which enabled us to use influent concentrations in the range of 500 ppm. This corresponds to 11% of the aqueous solubility of DCP (4500 ppm) at room temperature.

The modified clays were weighed and layered on top of 6-30 mesh unmodified emathlite and secured in place by glass wool. All the connections were made from 1/16 inch stainless steel tubing and appropriate fittings. The DCP reservoir (1 liter capacity) was made of glass. All adsorption experiments were carried out under a constant pressure head and the flow regulated by a control valve attached to the reservoir. The outlet was connected to an automated fraction collector. Pre-weighed scintillation vials were used to gather effluent samples for a fixed time period. Thus, the flow rate was measured gravimetrically.

Prior to the start of the adsorption experiment, the column was washed overnight with at least 1 liter of deionized water. The purpose was two-fold: one to allow the bed to settle and attain uniform permeability, and secondly to wash off any " desorbable " surfactant from the surface of modified clays. The wash sample was assayed for CPC and was found to contain no measurable amount of the surfactant.

The effluent and the influent DCP concentrations were determined by UV absorption spectrometry at 277 and 284 nm. A second wavelength was chosen because preliminary experiments indicated that DCP absorption at 277 nm was markedly affected by its passage through the column, especially CPC-EMAT. A calibration curve for DCP both at 277 and 284 nm was used to convert measured absorbances to solution phase concentration. A UV spectrum of DCP revealed that molar absorbance of DCP was nearly identical at 277 and 284 nm. The influent DCP concentration ranged from 0.54 - 0.56 mg/ml. Two flow rates of 0.5 and 0.8 ml/min were used. With a pore volume of 3.3 ml, the mean residence times were respectively 6.6 and 4.1 min. The influent concentration of DCP was measured before, during and at the end of each adsorption experiment.

After the end point of adsorption was reached, the adsorbent was carefully removed and the adsorbed DCP was back-extracted with neat methanol. In other cases, the column was washed with 1 liter of deionized water, and the amount of DCP in the wash water was determined. Subsequently, a fresh DCP solution was passed through the SAME column to monitor the extent of DCP adsorption. After each adsorption experiment, the adsorbent was dried, weighed and the amount of residual surfactant on the surface was assayed as described in section III. The results of packed bed adsorption of DCP are shown in Figs 1 - 5.

Adsorption of DCP on CPC-EMAT:

Figs 1 - 3 display the adsorption profiles of DCP on CPC-EMAT. The effluent DCP concentration is normalized with respect to the mean influent concentration. A strong adsorption is indicated by a delayed breakthrough and a slow rise to the end point of adsorption. The effluent data are plotted in terms of DCP absorbances at 277 and 284 nm. It can be seen that the 277 nm profile levels off below the influent value, while the 284 nm absorption band appears to become more intense. This feature is easily discernible in Fig. 2. The change in molar absorptivity may be related to a shift in the pK_a of the phenolic hydroxyl of DCP. The column effluent had a pH of 8.2 - 8.5, while the influent DCP solution had a pH of 7.3. Thus, it seems likely that the observed

Fig. 1 Adsorption of DCP on CPC-EMAT

Flow rate = 0.5 ml/min. Influent DCP Conc. = 0.56 mg/ml

Weight of CPC-EMAT = 3.0 g

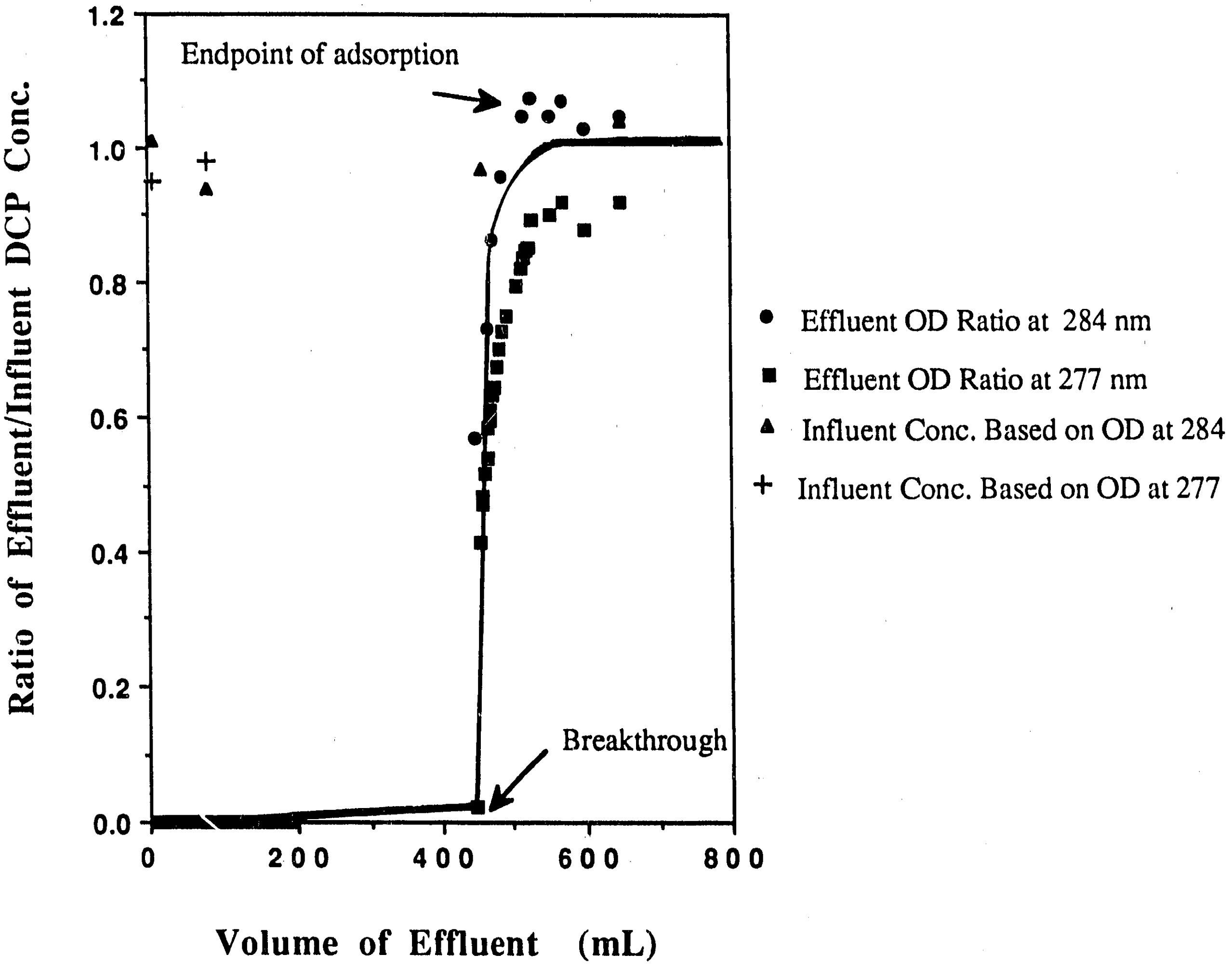

Fig. 2 Adsorption of DCP on CPC-EMAT ;Effect of Flow rate.

Flow rate = 0.8 ml/min.

Influent DCP Conc. = 0.55mg/ml

Weight of CPC-EMAT = 2.0 g

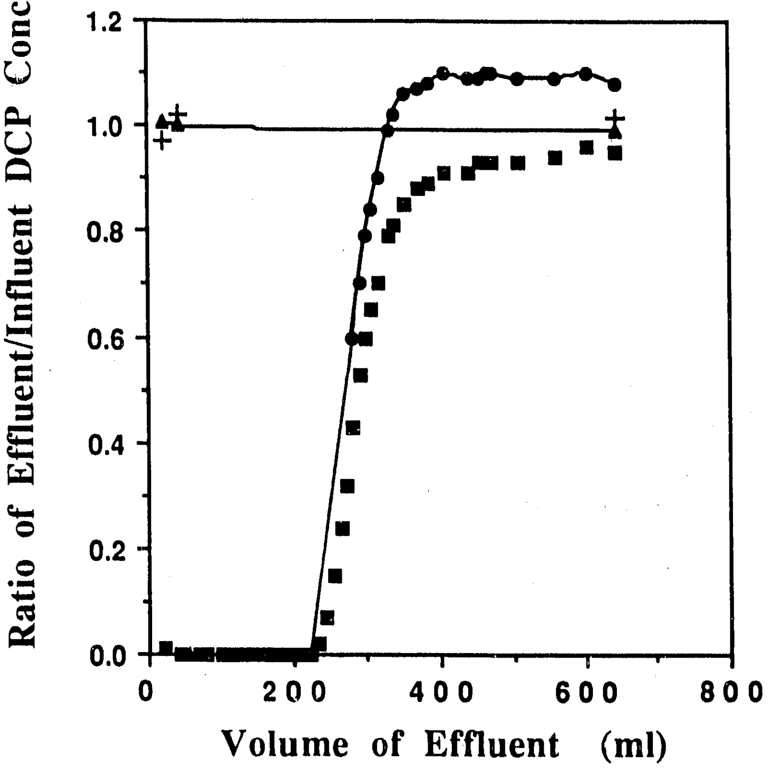

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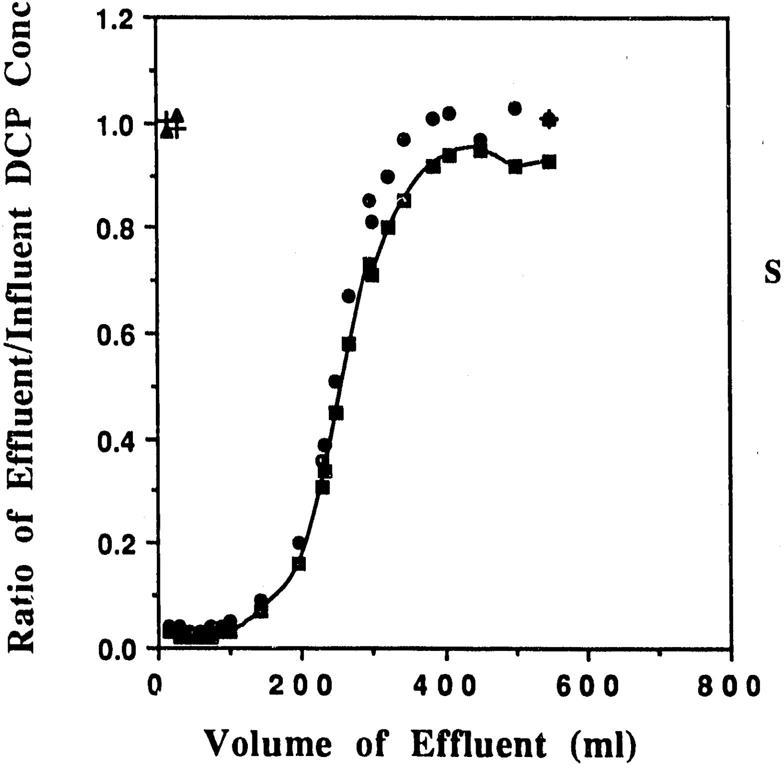
Fig. 3 Second Adsorption of DCP on CPC-EMAT

Experimental Conditions Same as Fig. 2



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shift in the molar absorbance of DCP may be related to the relative amounts of the protonated and deprotonated forms of DCP.

The adsorption of DCP appears to be independent of the flow rate within the range studied here. (Compare Figs. 1 and 2). Further, it appears that CPC-EMAT, partially regenerated by backwash with deionized water, re-adsorbs DCP as strongly as the virgin adsorbent (Fig. 3). But, the breakthrough point is not as well defined as in the other two cases. However, the total amount of DCP re-adsorbed is nearly equal to DCP desorbed with de-ionized water (see below). Thus, DCP adsorption appears to be quite reversible.

Mass Balance:

The effluent DCP was combined into fractions and the volumes and the DCP concentration in each one of these fractions were measured. The results for the adsorption of DCP onto CPC-EMAT are shown in Table 2.

TABLE 2

COLUMN No. & Adsorbent Weight	DCP Conc. Initial	DCP Adsorbed (mg)	DCP Desorbed (mg)	% Recovery
1; (3.0 g)	0.56 mg/ml	253.5 (84.5 mg/g)	263•	103.9
2; (2.0 g)	0.55 mg/ml	169.6 (84.8 mg/g)	136.2••	80.3
3; (2.0 g)•••	0.56 mg/ml	135.8	----	---

• Desorption was carried out with 50 ml of neat methanol.

•• Desorption was effected with approximately 1 liter of deionized water.

••• Adsorption was carried out on column 2 following desorption with deionized water.

The values given in parentheses are the specific adsorption density in units of mg DCP adsorbed/g adsorbent.

The results reported in Table 2 suggest that DCP adsorption onto CPC-EMAT is strong and reversible. Previously, we had reported an equilibrium adsorption capacity of 100mg DCP/g with CPC-MONT and CPC-HYDAL-MONT (12). Thus, the observed capacity of 85mg DCP/g CPC-EMAT represents a lowered sorption capacity due to a finite contact time between the adsorbate and the column. Secondly, it is worth noting that 80% of the adsorbed DCP can be eluted by backwashing with deionized water. This indicates that bulk of the adsorbed DCP is reversibly bound. This is further verified by the fact that the same column can re-adsorb DCP when it is once more brought into contact with a step input of DCP solution (Fig. 3 and Row 3, Table 2). However, the adsorption profile shown in Fig.3 reveals that the effluent DCP concentration prior to breakthrough is not zero, but a small positive value. It may be that a regenerated CPC-EMAT does not bind DCP as strongly as the virgin adsorbent. Finally, an organic solvent such as methanol can quantitatively extract DCP from the adsorbed state. This is due to the fact that DCP is more soluble in methanol than water.

Adsorption DCP onto CPC-HYDAL-MONT:

The adsorption of DCP onto CPC-HYDAL-MONT was carried out in an identical manner and the results are shown in Figs. 4 and 5. Fig. 4 represents DCP adsorption onto virgin adsorbent, and Fig. 5 is the adsorption profile on the regenerated column. The two striking differences between Figs. 1 - 3 and these two figs. are the occurrence of an early breakthrough and a slow rise to the end point of adsorption. In fact, on the regenerated column (Fig. 5), the adsorption profile levels off slightly below the end point. Secondly, the DCP absorption bands at 277 and 284 were found to be unmodified after the passage of DCP through the column. It was noted that the effluent pH was not significantly different from the influent pH. This latter difference may be due to the fact that montmorillonite is a research-grade clay, while EMAT is a commercial mixture which may have affected the acid-base behavior of DCP.

Mass Balance:

The packed bed adsorption experiment was analyzed in the same manner as was done with CPC-EMAT and the results are shown in Table 3.

TABLE 3

COLUMN No. & Adsorbent Weight	DCP Conc. Initial	DCP Adsorbed (mg)	DCP Desorbed (mg)	% Recovery
1; (1.3 g)	0.54 mg/ml	93.5 (71.9 mg/g)	71.0•	76.0
2; (1.3 g)	0.56 mg/ml	84.3	----	---

• Desorption was effected with approximately 1 liter of deionized water.

The values given in parentheses are the specific adsorption density in units of mg DCP adsorbed/g adsorbent.

DCP adsorption on CPC-HYDAL-MONT is as reversible as it was with CPC-EMAT. But, **the sorption capacity was lower than in the case of CPC-EMAT.** This is remarkable because the surfactant concentration on CPC-HYDAL-MONT was higher (17% by weight) when compared to CPC-EMAT(only 13% by weight). Secondly, the regenerated sorbent bound more DCP than was desorbed by solvent back-wash. This is being investigated.

The ability of regenerated CPC-EMAT and CPC-HYDAL-MONT samples to bind DCP as strongly as the virgin adsorbent indicated that the adsorbed surfactant did not " desorb " during the lengthy adsorption experiments lasting at least 2 - 3 days. This was checked by heating the adsorbents at 580^{0}C after the column experiments were completed. The observed weight loss was nearly the same as was noted with the virgin adsorbent. This established that there was no perceptible desorption of the adsorbed surfactant, once again confirming that surfactant-modified clays are structurally stable.

Fig. 4 Adsorption of DCP on CPC-HYDAL-MONT.

Flow Rate = 0.5 ml/min. Weight of CPC-HYDAL-MONT = 1.3 g

Initial DCP Conc. = 0.54 mg/ml.

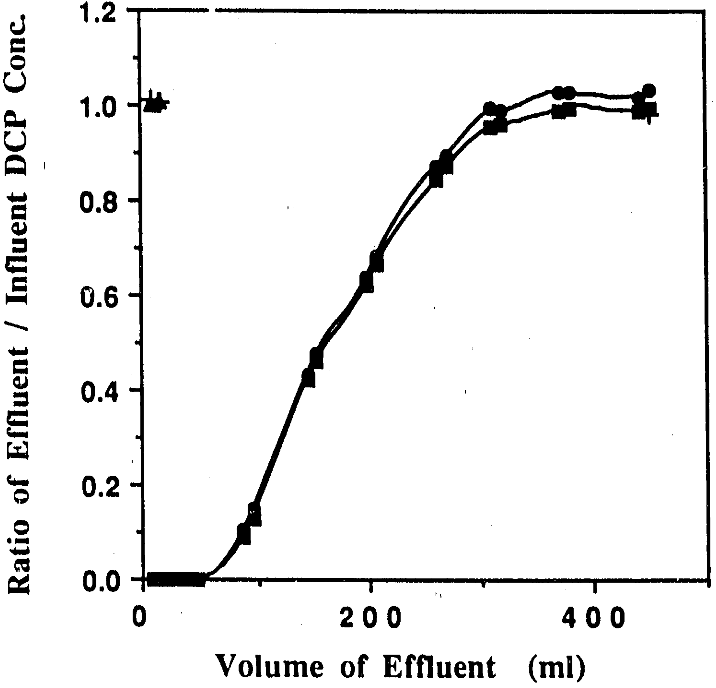

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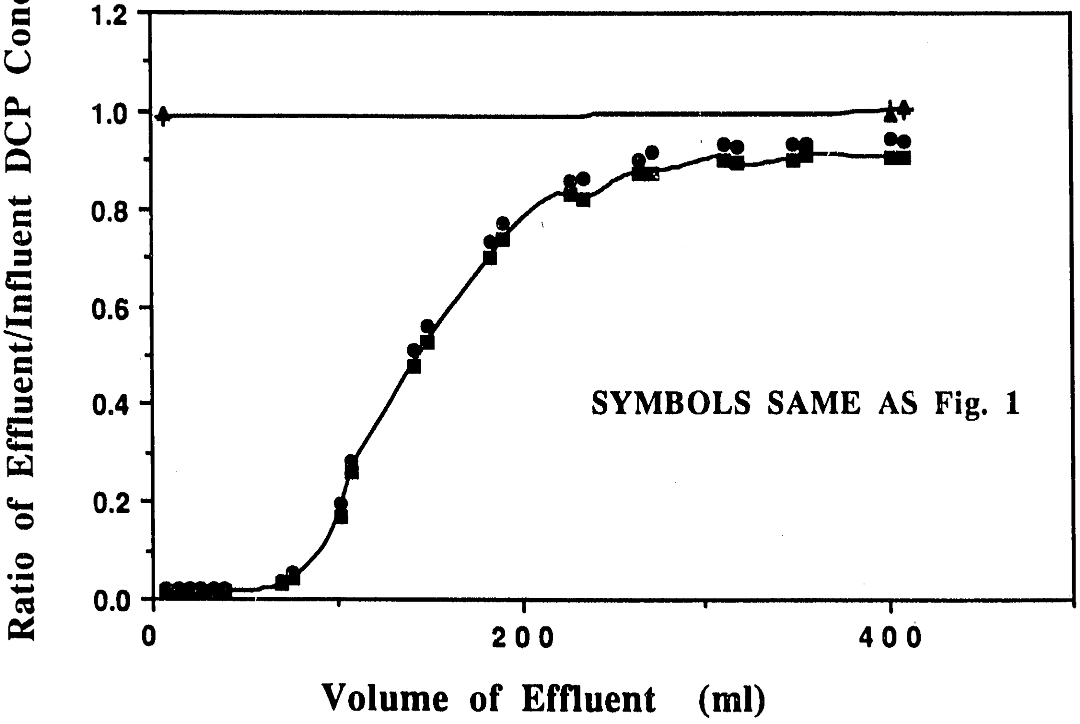
Fig. 5 2nd DCP adsorption onto CPC-HYDAL-MONT.

Experimental Conditions Same as in Fig. 4



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V. CONCLUSIONS:

(1) Clay modification procedures, developed in an earlier phase of the current project, have been successfully scaled-up to yield optimal amounts of modified clays. It was also shown that the scale-up can be accomplished with the commercial clay mixtures. A detailed analysis of the modified clays showed that the adsorbed surfactant was stable against desorption. The actual amounts adsorbed were also identical to our earlier results.

(2) Packed bed adsorption experiments demonstrated a strong, but reversible adsorption of DCP onto these modified clay columns. A major portion of the adsorbed DCP could be back-extracted with deionized water. The adsorbent, thus regenerated was found to be as effective as the virgin adsorbent.

(3) CPC-EMAT containing a lower amount of adsorbed surfactant (13% by weight) compared to CPC-HYDAL-MONT (17% by weight) had a larger sorption capacity for DCP. This finding confirms our earlier results that the absolute amount of surface organic carbon is NOT a major determining factor in the adsorption of toxic organics. Provided that a minimum amount of surface organic carbon is available, its ORIENTATION appears to be as important as the amount itself.

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