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QUARTERLY TECHNICAL REPORT:

Title:	WETLAND TREATMENT OF OIL AND GAS WELL WASTEWATERS
Contract No.	DE-AC22-92MT92010
Institution:	University of Michigan, Department of Chemical Engineering
Date:	April 2, 1993
Contract Date:	May 25, 1992
Anticipated Completion Date;	May 24, 1994
Government Award:	($ 80,727 for the First Year)
Project Director:	Prof. Robert H. Kadlec
Project Manager:	Dr. Keeran R. Srinivasan
PIs:	Prof. Robert H. Kadlec and Dr. Keeran R. Srinivasan
Technical Project Officer (COR):	Dr. Brent W. Smith
Reporting Period:	November 25, 1992 - Feb. 24, 1993.

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I. Executive Summary:

During the first quarter of the above contract, all the elements of Task 1 were completed. The first quarterly report (1) presented an overview of a wetland and its increasing use in industrial wastewater treatment. An idealized, reaction engineering description of wetlands was presented to demonstrate how the various processes that occur in a wetland can be modeled. Previous work on the use of wetlands to remove BOD, TSS, Phosphorus and Nitrogen was reviewed. Recent literature on the application of wetland technology to the treatment of petroleum-related wastewater was critically evaluated and an outline of the research plans for the first year was delineated. Further, our literature search (nominally completed under Task 1) unearthed more recent studies (some unpublished) and a summary was included in the second quarterly report (2). In the second quarterly report, results of our efforts on the construction of a laboratory-type wetland were also reported. Initial studies on the use of wetland amendments such as modified-clays and algae cells were presented and discussed (2).

- Adsorption of heavy metal ions, Cu^{2+}, and Cr(VI) onto soils drawn from the laboratory-type wetland built as a part of this contract has been undertaken and these results are presented and discussed in this quarterly report.

- A number of studies on the design and preparation of modified-clays for the adsorption of Cr(VI) and β-naphthoic acid (NA) has been carried out during this quarter and these are also described and discussed in this report. The choice of β-naphthoic acid (NA) as an ionogenic organic compound was made on the basis of a recent personal communication to the Project Director that NA is a major contaminant in many oil and gas well wastewaters (3).

II. Task 2A: Adsorption of Cu2+ and Cr(VI) to soil components of a Laboratory-type Wetland:

In our second quarterly report we described the construction of a laboratory-type green house. Before attempting to study the uptake of heavy metals and toxic organics by the entire microcosm, studies were initiated to examine the role of the soil components of our wetland in such sorption processes.

A soil mass of 4.7 g wet soil was dispersed in de ionized water to yield a soil slurry containing (on a wet basis) of 6.38 mg wet soil/ml slurry. The following are the properties of the soil used in the metal uptake study.

Moisture Content:	46.7 ± 2.3 %.
Organic Carbon Content:	12.7 ± 2.9 % by weight (on a dry weight basis).
pH of the soil slurry:	7.5 - 8.5.
Ionic Strength:	Not Determined

Equal volumes of soil slurry and metal solutions were mixed in a batch reactor and agitated for 40 hours. Solids were separated by centrifugation and the metals analyzed using Perkin-Elmer AS 3100 Flame AA spectrometer. Positive controls and blanks were included to account for losses, if any. All experiments were done in triplicates and the initial metal concentrations ranged (in both cases) from 1 - 20 mg/L. The results are shown in Figs 1 and 2 respectively for the case of Cu^{2+} and Cr(VI) adsorption

Fig. 1 Cu adsorption by wetland soil

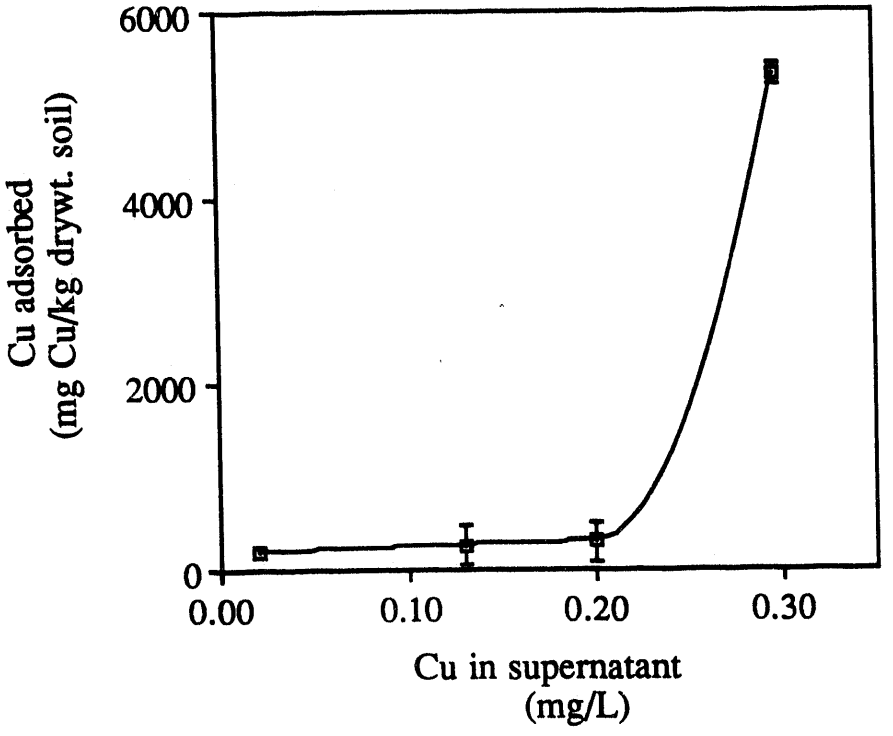
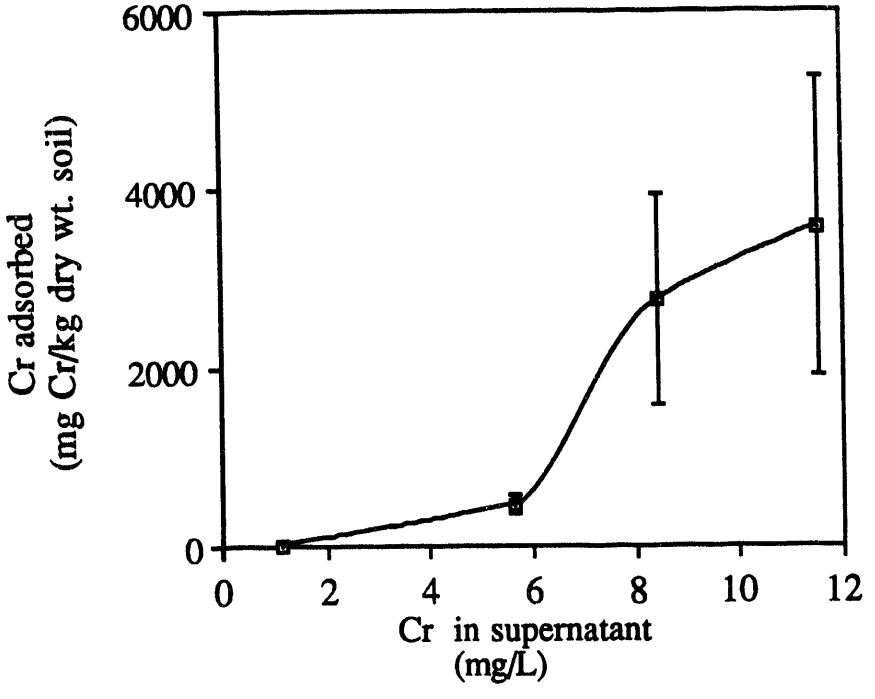


Fig. 2 Cr adsorption on wetland soil



It is clear from the results shown in Figs 1 and 2 that wetland soils had very little capacity or affinity for adsorbing either of the metal ions. The upswing in Cu adsorption at the highest initial concentration used (20 mg/L) suggests that some of the Cu ions may have precipitated onto soil surface at the alkaline pH of the slurry. At the highest initial Cu concentration, the positive controls showed a significant loss of Cu ions from solution. For example, only 50 % of the initial Cu^{2+} concentration (20 mg/L) was recovered in the supernatant after 40 hours of equilibration. This loss is attributed to possible hydrolysis and precipitation of Cu ions. These results seem to suggest that adsorption of cationic heavy metals such as Cu^{2+} by the soil component of a wetland is poor. Any uptake seems to involve hydrolysis and precipitation. This is in contrast to strong adsorption of Cu^{2+} ions to peat or modified clays (4,5).

The uptake of Cr(VI), the anionic heavy metal, is also quite weak. This is not surprising in view of the well known fact that soil surfaces are invariably negatively charged. The positive controls showed a much smaller amount of loss from solution and it is concluded that Cr(VI) ions are poorly adsorbed due to exclusion from the soil/solution interface because of electrostatic repulsion between the soil surface and the anionic Cr.

IV. Task 2B: Development of Wetland Amendments:

Modified-clays:

In the previous report (2) we reported on the development of a surfactant-modified smectite that was shown to adsorb Cu^{2+} and Cd^{2+} ions. The active component in our adsorption scheme was an alkyl diamine, Duomeen-T, DT. In this report, we describe how the same alkyl diamine has been used to adsorb Cr(VI) and β-naphthoic acid from their respective aqueous solutions.

Preparation of MONT-DT:

Duomeen-T, (DT), is a commercially available, aliphatic diamine of the type (R-NH-$(CH_2)_3$-NH_2;). This alkyl substituted, 1,3-diamino propane is supplied by Akzo Chemicals and the size of the alkyl group ranges from C12 to C18. The apparent molecular weight based on hydrocarbon assay is 350 g/mole (6). Duomeen-T, (DT), is insoluble in water and a solution of DT was prepared in isopropanol for use.

Montmorillonite (SWy-1) was obtained from the Clay Minerals Society Repository and a size fraction < 2μm in size was cleaned to remove carbonates by treatment with Na acetate/acetic acid buffer at pH 3.8. The treatment was continued by exchanging the counter ions on the clay with Na ions using 1.0 M solution of the latter. Following Na exchange, the clay was washed with de ionized water until the supernatant was free of Cl^- ions (as determined by the $AgNO_3$ test). The resultant suspension was freeze-dried for later use.

A suspension of Montmorillonite (5 g; 3.85 meq of total charge, assuming a cation exchange capacity of 0.77 meq/g montmorillonite) was reacted with DT (5.355 g corresponding to 15.3 mmoles or 30.6 meq of charge when both the amine functions are fully protonated) at pH 6.0. The charge ratio between clay and DT was 1:8. The clay-DT suspension was continuously mixed and heated to 50^0C for 2 hours. The reaction was continued at room temperature overnight with continuous mixing. The following exchange reaction was expected to occur:

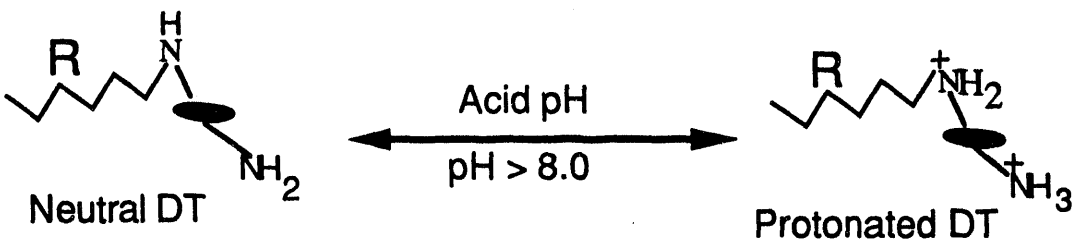
MONT-Na + DT = MONT-DT + Na

The MONT-DT suspension was washed extensively with de ionized water adjusted to pH 3.0, following which, it was vacuum dried at 60^0C for 10 hours and oven-dried at 105^0C overnight.

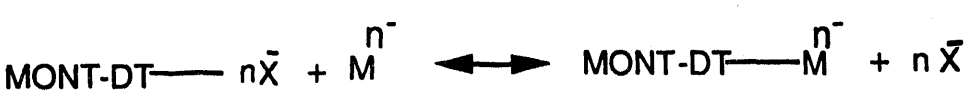
Properties of MONT-DT:

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

The above results indicate that almost all of DT reacted and formed a coating of DT over montmorillonite particles. Thus, a super equivalent adsorption of DT appears to have occurred and the surface of MONT-DT has become positively charged as a consequence, enabling MONT-DT to adsorb Cr(VI) and β-naphthoic acid by anion exchange. Anion exchange reaction of MONT-DT is as follows:



(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

Experiments were conducted to study the uptake of Cr(VI) as a function of pH. A 1000 ppm stock solution of Cr(VI) was prepared and an aliquot was diluted to a final concentration of 20 ppm in Cr(VI) in various buffer systems ranging from 3.0 to 9.0. A slurry of MONT-DT at 1 mg/ml was added to determine the extent of Cr(VI) adsorption after 24 hours of mixing. Controls (i.e solutions containing identical Cr(VI) concentrations with no added adsorbent) were used to account for losses of Cr(VI) by processes other than adsorption to the modified-clay.

Fig. 4 Cr(VI) Adsorption onto MONT-DT: pH Effect

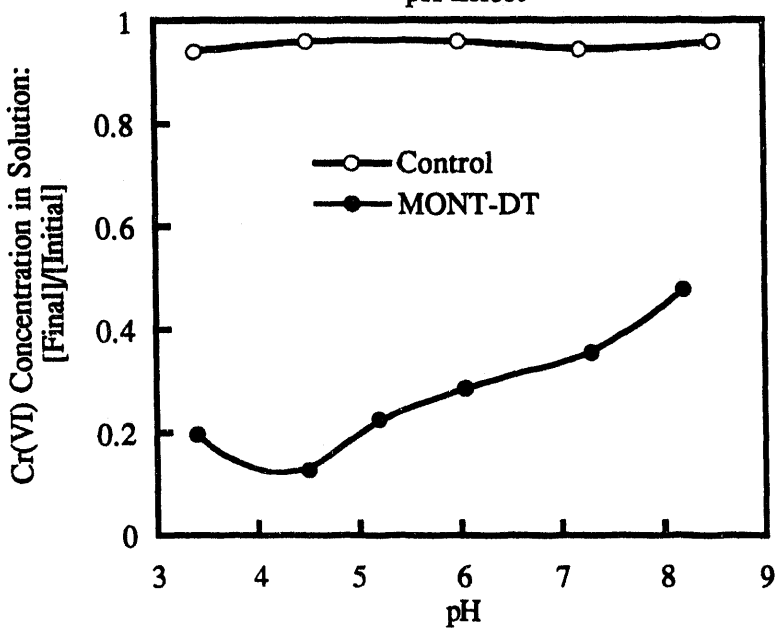
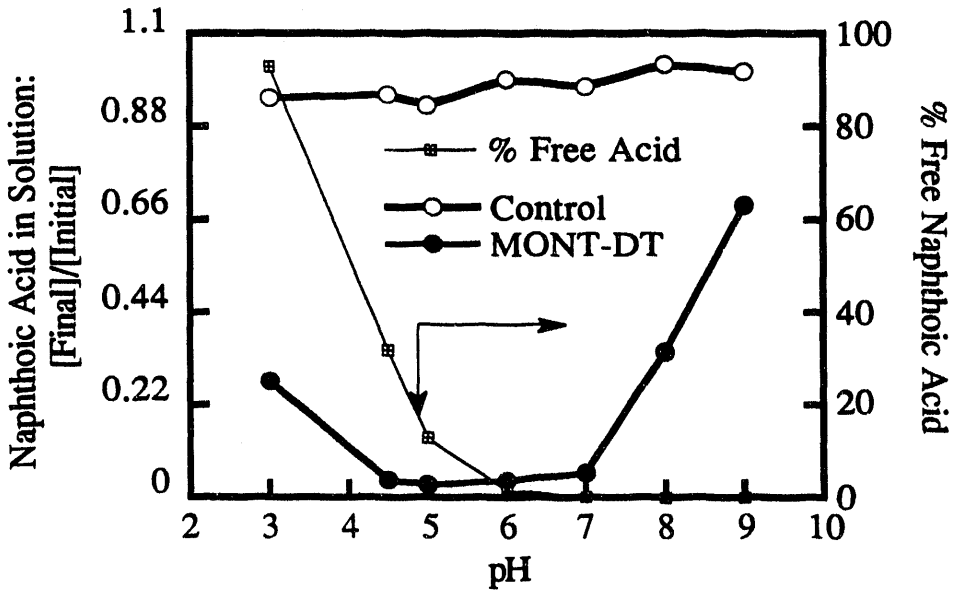


Fig. 5 Adsorption of Naphthoic Acid onto MONT-DT: pH Effect



Similar measurements on the uptake of β-naphthoic acid as a function of pH were also carried out. A stock solution of 50 ppm was prepared, from which the initial NA concentration of 5 ppm was obtained by dilution with buffer. The properties of β-naphthoic acid are listed below:

Aqueous solubility:	70 ppm
pKa (7):	4.17

The results of Cr(VI) and b-naphthoic acid adsorption onto MONT-DT are shown in Figs 4 and 5.

It is clear from Fig. 4 that Cr adsorption follows the pH-dependent charging characteristics of MONT-DT as shown in Fig. 3. At low pH both the amine groups on DT are protonated and the positive charge facilitates Cr(VI) adsorption. As the pH increases the extent of positive charge on the surface decreases due to the deprotonation of the amine groups on DT, thereby reducing the amount of Cr(VI) adsorption.

β-naphthoic acid, on the other hand, can adsorb onto MONT-DT by two mechanisms: hydrophobic partitioning and anion exchange. The latter mechanism appears to be the dominant one because, at higher pH (above pH 8.0), the amount of free acid in solution is almost zero (see the right panel, Fig. 5). A much weaker adsorption of naphthoic acid is observed at pH 8.0 and higher. Some sorption onto hydrophobic patches on MONT-DT can not be, however, excluded. Thus, hydrophibic partitioning may be responsible for the residual sorption capacity of MONT-DT for NA at high pH.

V. Future Work:

The screening tests described above will be followed by the measurement of adsorption isotherms for Cr(VI) and β-naphthoic acid on MONT-DT at various pH. Interaction of different components of a wetland system with β-naphthoic acid will be studied. Further work on the immobilization of toxic organics and heavy metals by modified-clays, uptake of different types of heavy metals by algae, biodegradation of toxic organics by the microorganisms inherent to a wetland and the sorption of heavy metals by the sedimentary components of a wetland are some of the study areas for the next reporting period.

VI: SUMMARY

This quarterly report presents results from studies on the adsorption of heavy metal ions, Cu^{2+}, and Cr(VI) onto soils drawn from the laboratory-type wetland built as a part of this contract. Both Cu(II) and Cr(VI) are weakly adsorbed by the soil components of the wetland. A new type of modified-clay, designated MONT-DT, has been prepared and the adsorption of Cr(VI) and β-naphthoic acid (NA) onto MONT-DT has been carried out. Both the compounds are strongly adsorbed by MONT-DT at pH 4.5 and the extent of adsorption decreases at pH above 8.0. It is concluded that anion exchange is the dominant mechanism of adsorption for both the pollutants.

VII: Report Distribution List:

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VIII. REFERENCES:

(1) R. H. Kadlec and Keeran R. Srinivasan: 1st Quarterly Report, U. S. DOE, PETC, August, 1992.

(2) R. H. Kadlec and Keeran R. Srinivasan: 2nd Quarterly Report, U. S. DOE, PETC, November, 1992.

(3) J. R. Gulley and P. G. Nix: " Wetland Treatment of Oil sands Operation Wastewater " (A private Communication from authors to R. H. Kadlec, PI).

(4) P. Eger and K. Lapakko: " Use of wetlands to Remove Nickel and Copper from Mine Drainage " in " Constructed Wetlands for Wastewater Treatment " (ed.) Donald A. Hammer, Lewis Publishers, Chelsea, MI, pp 780 (1989).

(5) Keeran R. Srinivasan and H. Y. Wang: " Removal and Recovery of Heavy Metals from wastewaters using Modified-clays", a Manuscript Submitted to the 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.

(6) Akzo Chemie America: Bulletin 85-1, " Specification and Properties of DUOMEEN Diamines and Diamine Salts", An Armak Chemical Publication, (1985).

(7) Handbook of Chemistry and Physics: Weast 57th Edition; CRC Press (1976-77).

IX. Publications: None

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