AIIM

Centimeter

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 mm

1 2 3 4 5

Inches

1.0

4.5 2.8 2.5
5.0
5.6 3.2 2.2
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8.0 4.0 2.0
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1.25 1.4 1.6

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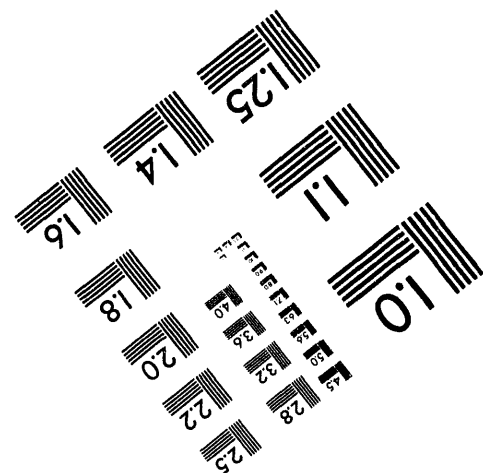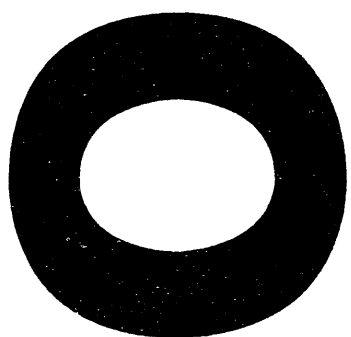
QUARTERLY TECHNICAL REPORT:

Title:	WETLAND TREATMENT OF OIL AND GAS WELL WASTEWATERS
Contract No.	DE-AC22-92MT92010
Institution:	University of Michigan, Department of Chemical Engineering
Date:	June 22, 1994
Contract Date:	May 25, 1992
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Government Award:	
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:	March 25, 1994 - May 24, 1994.

DISCLAIMER

MASTER

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 waste water 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 waste water 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 Further, our literature search (nominally completed under Task 1) unearthed more recent studies (some unpublished) and a summary was included in the second quarterly report (2).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). In the third quarterly report (3), adsorption of heavy metals ions such as Cu(II) and Cr(VI) onto soils drawn from the laboratory-type wetland (LW) was shown to be weak. On the other hand, it was shown that modified-clays did adsorb Cr(VI) ions strongly at pH 4.5. Further, studies on the pH dependence of the adsorption of β-naphthoic acid, (NA), a well-documented contaminant in many oil and gas well waste waters (4), onto modified-clays were undertaken and it was shown that uptake of NA by modified-clays was of the high affinity type at pH 4.5 and 7.0, but weak at pH 9.0. Adsorption of heavy metal ions, Cu^{2+}, and Cr(VI) onto algae, a proposed wetland amendment, was carried out and the results were presented and discussed in the fourth quarterly report (5). Uptake of NA by the soil component of LW was monitored as a function of pH. The adsorption of NA onto modified-clays was studied in greater detail and these data were described and analyzed in an earlier quarterly report (5). Studies on the dynamics of uptake of phenol and NA by laboratory-type wetlands (LWs) were initiated and preliminary results indicated that both phenol and NA were sorbed onto components of LWs (6). It was also observed that phenol volatilization from supernatant water contributed to phenol disappearance. This was attributed to high water temperature during the Summer months when these studies were conducted. On the other hand, there was minimal loss of NA through evaporation even during Summer months(6). Further results from studies on the uptake of Cu(II) and phenol by laboratory-type wetlands (LWs) designed and built during the earlier phases of this study have also been considered. The uptake of Cu(II) by laboratory-type wetland was shown to follow a tri-phasic behavior attributed to partial hydrolysis and precipitation , sorption onto wetland components and a slow dispersion into underlying pore water of the laboratory-type wetland (7). The addition of peat was observed to have only a minimal effect on Cu(II) uptake. Phenol sorption, however, was favorably modified by the addition of peat. Furthermore, a lower water depth in the laboratory-type wetland resulted in slightly higher evaporative loss of phenol, but the major removal mechanisms of phenol appeared to be sorption to various components of a laboratory-type wetland and degradation by micro organisms inherent to the wetland.

A mass balance model was developed to quantify the fate of phenol in LWs. The model was based on the postulate that the fate of phenol in LWs could be attributed to a combination of (1) evaporation of solute and solvent, (2) adsorption of phenol onto various components of LW and (3) its biodegradation, both in solution and at solid-liquid interface. As an initial approximation, the latter two processes were lumped together and incorporated into the model as an unit operation. Both zero order and first order kinetics for the disappearance of phenol were considered. Evaporative losses of water and phenol were taken into account and this model was presented and discussed in the previous quarterly report (8). Further, The dynamics of the uptake of Cr(VI) by laboratory-type wetland systems (LWs) was studied and the results were presented and discussed (8).

•   In the present report, the simultaneous uptake of Cu(II) and Cr(VI) by LWs has been considered. Two different molar ratios (Cu(II/Cr(VI)) of **3.8 and 0.46** have been used. Since most of oil and gas waste wasters are known to contain both cationic and anionic heavy metals in the dissolved form, a study of simultaneous uptake of cationic and anionic heavy metals will be helpful in the design and construction of a wetland treatment system for such waste waters.

II   Task 3:   Simultaneous Uptake of Cu(II) and Cr(VI) by LWs:

In a previous report (2), we had described the design and the construction of a laboratory-type wetland. Briefly, 18-gallon plastic containers containing 4 cattails/container were prepared in a suitable soil matrix and grown at the Botanical Gardens operated by The University of Michigan. The following are the steps we have used to quantify simultaneous uptake of Cu(II) and Cr(VI) by LWs.

(1)   Removed the overlying water and replaced with fresh tap water. In some cases, 2-3 gallons of peat in the form of a thick paste were layered before adding tap water. Water depth was set to an average of **5.5 ± 0.6** inches from the surface of the soil matrix.

(2)   After 24 -hr equilibration, the height of the water column was monitored again and the overlying water was spiked with **Cu(II)** and **Cr(VI)** to a pre-determined nominal concentration at two different molar ratios of **3.8 and 0.46** to avoid precipitation of heavy metal ions under stoichiometric conditions. Following the addition of the heavy metals, the water was mixed manually with a paddle, and was left undisturbed thereafter.

(3)   Collected water samples prior to the start of the experiment and periodically during the experiment. The temperature, water depth and the pH were noted.

Concentrations of Cu (II) and Cr(VI) were measured using Perkin Elmer AA Spectrometer. Both Cu(II) and Cr(VI) uptake experiments were studied in duplicate. Water depth was maintained at the initial value of 5.5 inches and the pH was between 5.5 - 6.5 and did not change during the course of the experiment. The details of experimental conditions are given in Table 1.

Table 1:   Details of Experimental Conditions:

LW # and Volume of overlying water (L)		Cu(II) Added (mmoles)	Cr(VI) Added (mmoles)	Cu(II)/Cr(VI) Ratio	
44;	39.7	4.4	1.2		3.7
13;	29.7	4.4	1.12		3.9
				Mean:	**3.8**
36;	33.4	1.59	3.4		0.47
56;	37.5	1.54	3.4		0.45
				Mean:	**0.46**

Fig. 1 Removal of Cr(VI) by Laboratory-type Wetland
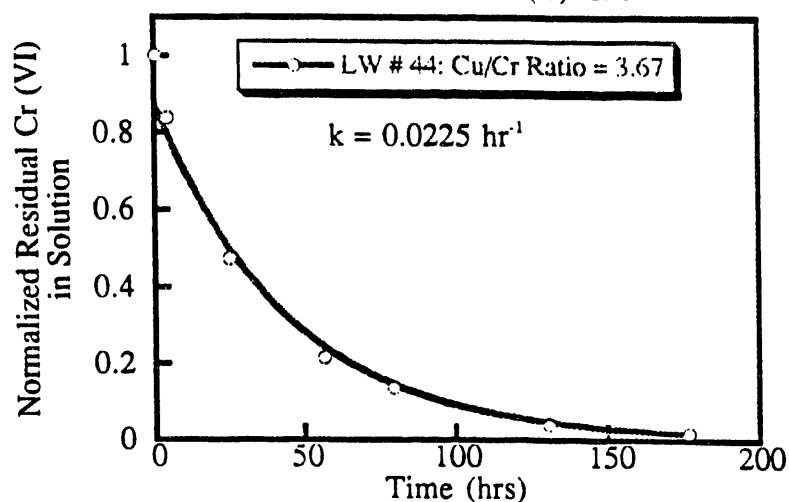in Presence of Cu(II) ions

Fig. 2 Removal of Cr(VI) by LWs in Presence of Cu Ions:
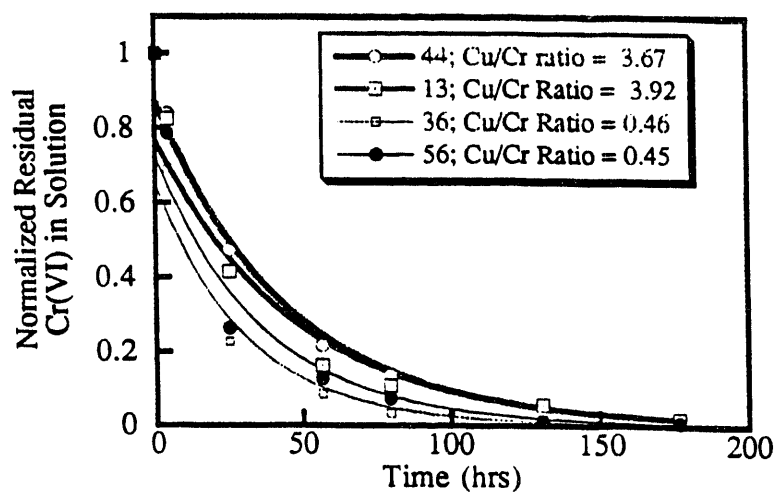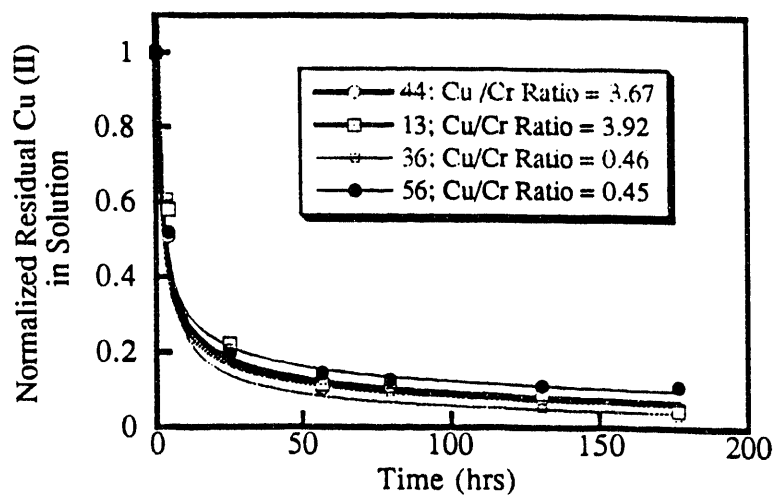Effect of Cu/Cr Ratio

Fig. 3 Removal Cu(II) Ions by LWs in Presence of Cr (VI):
Effect of Cu/Cr Ratio

Suitable controls were used to account for losses of heavy metal ions due to non specific processes. The results are shown in Figs 1, 2, and 3.

In Fig. 1, the extent of removal of Cr(VI) by LW # 44 in presence of a high level of Cu(II) ions is shown. The data could be fitted to an exponential function with a first order rate constant of 0.0225 hr^{-1}. It is worth noting that our earlier work on the uptake of Cr(VI) by LWs showed a similar exponential dependence with time when only Cr (VI) was present in the system (7). Thus, it would appear that the presence of excess of Cu(II) ions has no measurable effect on Cr(VI) removal by LWs. This is verified by the results shown in Fig. 2 which summarizes all the results on the effect of Cu(II) ions in solution. At a high Cu/Cr ratio, the first order removal of Cr is slightly slower than at low Cu/Cr ratios. To quantify this effect, The data shown in Fig. 2 were fitted to exponential functions of the form:

$$[Cr(VI) (t)]/[Cr(VI)(0)] = exp(-kt)$$

and the respective rate constants were calculated. These are summarized in Table 2.

Table 2:   Kinetic Constants for Cr(VI) Uptake by LWS in presence of Cu(II):

Cu/Cr Ratio	k (hr^{-1})	t$_{1/2}$ (hrs)	r^2 of the fit
3.67	0.0225	30.8	1.000
3.92	0.0213	32.5	0.98
0.46	0.033	21.0	0.98
0.45	0.028	24.8	0.98

It can be seen from Table 2 that low Cu/Cr ratio leads to faster decay of solution phase Cr (VI) concentration. Since Cr(VI) is highly soluble at the operating pH, the observed differences in the first order rate constants are attributed to variable characteristics of LWs. It can be concluded, however, that the average half life of Cr(VI) in LWs is of the order of **25 hours.**

The removal of Cu(II) in presence of Cr(VI) shows a biphasic behavior; a rapid initial phase, followed by a slower second phase. These results are displayed in Fig. 3. The data were fitted to a power law function of the form:

$$[Cu(II)(t)]/[Cu(II)(0)] = a . (t^{-n})$$

where " a " is a constant and " n" is the power law exponent. The power law fit of the data is strictly empirical in nature which, however, yields a useful, functional relationship between residual Cu(II) concentration vs time. The details are shown in Table 3.

Table 3:   Constants for Cu(II) Uptake by LWS in presence of Cr(VI):

Cu/Cr Ratio	n	t$_{1/2}$ (hrs)	r^2 of the fit
3.67	0.5	2.86	0.99
3.92	0.5	3.24	0.97

| 0.46 | 0.63 | 3.30 | 0.94 |
| 0.45 | 0.40 | 3.14 | 0.99 |

Using the values of " a" obtained from the curve fit half lives were calculated by inverting the above equation and these are listed in Table 3. The half lives for Cu(II) removal are approximately an order of magnitude lower than in the case of Cr(VI) removal. Secondly, the half life is independent of the **initial Cu(II) concentration (30 and 6 ppm)** or the **Cu/Cr ratio**. This observation leads us to conclude that rapid removal of Cu(II) is most likely facilitated by adsorption onto suspended particulate matter in LWs by cation exchange. Hydrolysis of Cu(II) followed by precipitation would have shown a significant dependence on initial Cu(II) concentration, which was **not observed** experimentally. In a previous report (7), we had identified three removal mechanisms for Cu(II), namely,

(1)   Hydrolysis and precipitation

(2)   Adsorption onto various components of a LW

(3)   Dispersion into the underlying pore space of a LW.

In light of the more extensive results obtained in the present study, a biphasic removal mechanism appears more reasonable. Processes (1) and (2), to varying degrees, represent the first phase of Cu(II) removal while the slower phase is most likely dominated by diffusive dispersion of Cu(II) into the underlying pore water of a LW.

Further, it was noted that the water samples drawn from the LWs contained small particles in suspension and that re-dispersion of these particles gave higher readings for metal ion concentration. The clear supernatant obtained after the particles had settled yielded once again lower values of residual metal ion concentration.

III.   Future Work:

Based on above results, a mass balance model will be developed to quantify metal uptake by LWs. This model will include effects of adsorption, hydrolysis and precipitation and diffusive dispersion.

IV: SUMMARY

This quarterly report presents results on the **simultaneous** uptake of Cu(II) and Cr(VI) by LWs from a binary mixture of the two ions. Non-stoichiometric mixtures of metal ions have been used to minimize precipitation. The uptake of Cr(VI) in presence of Cu(II) by laboratory-type wetland systems (LWs) follows first order kinetics with an average half life rf **25 hours** irrespective of the initial Cu/Cr ratio. On the other hand, Cu(II) removal is more complex with an average half life of only 3 hours.

V: Report Distribution List:

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VI. 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)   R. H. Kadlec and Keeran R. Srinivasan: 3rd Quarterly Report, U. S. DOE, PETC, March, 1993.

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

(5)   R. H. Kadlec and Keeran R. Srinivasan: 4th Quarterly Report, U. S. DOE, PETC, July, 1993.

(6)   R. H. Kadlec and Keeran R. Srinivasan: 5th Quarterly Report, U. S. DOE, PETC, October, 1993.

(7)   R. H. Kadlec and Keeran R. Srinivasan: 6th Quarterly Report, U. S. DOE, PETC, December, 1993.

(8)   R. H. Kadlec and Keeran R. Srinivasan: 7th Quarterly Report, U. S. DOE, PETC, March, 1994.

VII. Publications: None

SUMMARY: *(over)*

Constructed wetlands are small, on site systems that possess three of the most desirable components of an industrial wastewater treatment scheme: low cost, low maintenance and upset resistance. In the two years of the contract (just concluded), all the tasks indicated in the original statement of work (SOW) have been completed and the knowledge base of wetland treatment systems has been extended to include processes and substances of particular importance to small, on site systems receiving **oil and gas well waste waters**.

In Task 1, a list of the most relevant and comprehensive publications (29 in all) on the design of wetlands for water quality improvement was compiled and critically reviewed. Based on our literature search and conversations with researchers in the private sector, toxic organics such as phenolics and β-naphthoic acid, (NA), and metals such as Cu(II) and Cr(VI) were selected as target adsorbates.

In Task 2A, a total of 90 lysimeters equivalent to a laboratory-type wetlands (LWs) were designed and built to monitor the uptake and transformation of toxic organics and the immobilization of metal ions. In Task 2B, smectitic clays (hectorite and montmorillonite) modified by alkyl diamine-type and quaternary ammonium-type surfactants were shown to adsorb strongly metal ions (Cu(II) and Cr(VI)) and toxic organics such as β-naphthoic acid (NA). The surfactant-modified clays are expected to act as inexpensive additives to a wetland to enhance its sorption potential for a number of pollutants, organic and inorganic. Similarly, metal uptake studies with unicellular green alga, *chlorella vulgaris*, were undertaken to evaluate the ability of algae to enhance the metal uptake potential of wetlands.

In Task 3, studies on the uptake and transformation of toxic organics (phenol and NA) and the immobilization of metal ions (Cu(II) and Cr(VI)) by the laboratory-type wetland (LWs) have been completed. A kinetic model to quantify the transformation of phenols by LWs has been developed and applied to data from LWs.

During the no-cost extension period of the contract (through September, 1994) design parameters for a pilot wetland system will be evaluated and the project final report (PFF) will be prepared and submitted.

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