TRACE METAL REMOVAL FROM AQUEOUS SOLUTION

EDITED BY R. THOMPSON

Trace Metal Removal from Aqueous Solution

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R. Thompson
Borax Holdings Ltd, Chessington

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Preface

Increasing industrialisation brings with it the twin problems of more thorough removal of unwanted and possibly toxic metals from chemical and nuclear process effluent, and the need to obtain some metals from progressively leaner initial sources or dilute recycle liquor. Legislation and economics link the two, but whatever the motivation the chemical principles are the same.

Traditional methods such as precipitation by liming, cementation or electrodeposition become less effective as metal ion concentrations fall to the low parts per million range and large volumes of liquor need to be handled. Resort may be made to ion-exchange and solvent extraction procedures, but resin degradation and evaporation losses can add to the problems of an unattractively high proportion of aqueous phase.

Alternative methods based on biological systems, with the complexation abilities of large molecules, the use of novel membranes and selective precipitants which overcome previous solubility product barriers are constantly under development. A symposium reviewing progress in these fields was considered a fitting contribution by Industrial Division to the Society's 1986 Annual Congress held at the University of Warwick. The eleven papers presented, including two on analytical techniques now available for metal determination at trace levels, are reproduced here together with a subsequently contributed item on carbon adsorption techniques for gold recovery.

Raymond Thompson
Immediate Past President, Industrial Division

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Recovery of Heavy Metals by Immobilized Algae

By D.W. Darnall,* B. Greene, M. Hosea, R.A. McPherson, M. Henzl, and
M.D. Alexander

DEPARTMENT OF CHEMISTRY, BOX 3C, NEW MEXICO STATE UNIVERSITY, LAS CRUCES,
NEW MEXICO 88003, USA

INTRODUCTION

The binding of metal ions to microorganisms and the
application of this phenomenon to water treatment are rapidly
growing areas of interest. A survey of the scientific litera-
ature reveals two distinct approaches to the problem: (1) use
of living organisms and (2) use of a nonviable biomass. Metal-
ion binding to living cells can occur either through surface
adsorption or intracellular accumulation. This assertion is
supported by work which showed that uptake of metal ions by live
cultures cannot be accurately described by a model which assumes
adsorption only to the cell surface.[1] Metal-ion binding to
non-viable cells, however, is presumed to occur exclusively
through surface adsorption.

A number of workers have investigated the feasibility of
using actively growing algae in ponds or lagoons for wastewater
treatment[2-10]. The basic approach has been to flow polluted
waters through a lagoon in which an algal bloom is present. The
effluent waters from such a system are then found to have
lowered heavy metal ion concentrations. There are significant
practical limitations to methods which employ living algal

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systems. Perhaps the most significant limitation is that algal
growth is inhibited when the concentrations of metal ions are
too high or when significant amounts of metal ions are sorbed by
the algae.

Methods for water-treatment that employ non-viable cells
are not complicated by the problem of attempting to maintain
growth under adverse circumstances. In fact, Horikoshi et
al. [11] found that heat-killed cells display a binding capacity
for U(VI) three times greater than that measured for living
cells. Instead, the biomass is treated merely as another
reagent, a surrogate ion-exchange resin. The binding, or
biosorption, of metal ions by the biomass results from
coordination of the ions to various functional groups in or on
the cell. These chelating groups--contributed by carbohydrates,
lipids and proteins-- include carboxyl, carbonyl, amide,
hydroxyl, phenolic, imidazole, phosphate, amino, thiol, and
thioether moieties.

Tsezos et al. [12-16] studied the binding of U(VI) and Th(IV)
to non-living Rhizopus arrhizus, a common fungus. They proposed
that both ions are bound initially to amino groups present in
chitin. The resulting complex then hydrolyzes, and forms
insoluble hydroxy species which precipitate in pores on the cell
surface.

Ferguson and Bubela[17] examined the biosorption of Cu^{2+},
Pb^{2+} and Zn^{2+} to frozen or freeze-dried preparations of
Ulothrix, Chlamydomonas and Chlorella vulgaris. The degree of
binding they observed was greater at pH 7 than at pH 3. They
found that NaCl and $Mg(NO_3)_2$ inhibited only the binding of zinc,
suggesting that selective adsorption of Pb^{2+} or Cu^{2+} was
possible.

Nakajima et al. [18] studied the binding of various ions to freeze-dried Chlorella regularis. They observed relatively selective accumulation of ions from an equimolar solution (1.0 mM in each ion at pH 5.0) which decreased in the following order:

$$UO_2^{2+} > Cu^{2+} > Zn^{2+} > Ba^{2+} = Mn^{2+} > Cd^{2+} = Sr^{2+}$$
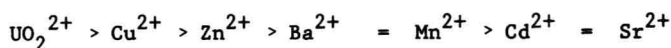
The removal of UO_2^{2+} was unaffected by the presence of other ions, but Cd^{2+} uptake was strongly inhibited by equal concentrations of UO_2^{2+} or Cu^{2+}. The same authors also described a procedure for immobilizing C. regularis in polyacrylamide for use as a chromatographic matrix.

If there is a single major conclusion to be drawn from our work to date, it would be that the surface of the alga, Chlorella vulgaris, is literally a mosaic of metal-ion binding sites--sites which differ in affinity and specificity. Both anions and cations can be bound. There are sites with high affinity for "hard" metal ions such as Al^{3+} and Fe^{3+}, and there are sites with equally high affinities for such "soft" ions as Hg^{2+}, Ag^+ and Au^{3+}.[19] Selectivity can sometimes be gained by judicious manipulation of solution parameters. For instance, chromate/dichromate, bound negligibly at pH values around neutrality, can be bound completely at pH 2.0. This binding site diversity gives the algae a broad applicability not found in conventional ion-exchange resins. A second major advantage we have discovered with the algae is that, in contrast to many conventional resins, the cells have relatively little affinity for Ca^{2+} and Mg^{2+}. Thus, in hard-water treatment applications, the algae will be less prone to saturation by these non-toxic ions.

RESULTS AND DISCUSSION

pH Dependence of Metal Ion Binding.

We have found that metal ions can be divided into three classes based upon the pH dependence of binding to the algae. The first class is comprised of metal ions which are tightly bound at pH $\geq$ 5 and which can be stripped (or are not bound) at pH $\leq$ 2 (19). Many ions fall into this class: Al^{+3}, Cu^{+2}, Pb^{+2}, Cr^{+3}, Cd^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2}, Fe^{+3}, Be^{+2} and UO_2^{2+}. The second class is comprised of metallic anions which display the opposite behavior of class I metal ions, i.e., they are strongly bound at pH $\leq$ 2 and weakly bound or not bound at all at pH values near 5. Ions in class II include $PtCl_4^{-2}$, CrO_4^{-2}, and SeO_4^{-2}. The third class of metal ions includes those metal ions for which there is no discernible pH dependence for binding and includes Ag^+, Hg^{+2} and $AuCl_4^-$. These three ions are the most strongly bound of all metal ions tested. Figure 1 illustrates data for the three classes of metal ions.

The data in Figure 1 were collected by incubating Chlorella cells (5 mg/ml) in 0.1 mM solutions of the metal ions in 0.05M
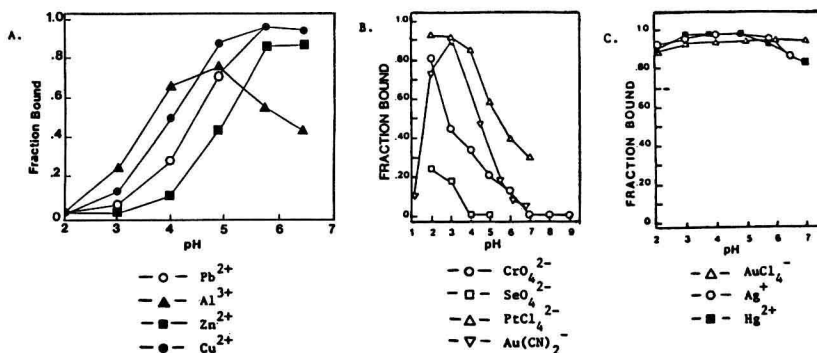

Figure 1.   The pH Dependence of Metal Ion Sorption by Chlorella vulgaris

acetate buffer. The buffer was added to maintain accurate pHs between pH 4 and 6. Because acetate is a good ligand for many of the metal ions, even increased binding is observed in the absence of the buffer. Furthermore, complete binding of metal ions in all three classes is obtained when solutions are passed through columns containing the immobilized algae rather than by simply incubating the algae in metal-containing solutions.

We believe that the different pH binding profiles for the three different classes of metal ions are a result of the nature of the chemical interactions of each class of metal ions with the algal cells. The pH profile for Class I metal ions is consistent with the metal cation being the species which is bound to ligands on the cell wall. At pH values above the isoelectric point of the cells there is a net negative charge on the cells. The ionic state of such ligands as carboxyl, phosphate, imidazole and amino groups will be such as to promote reaction with metal ions. As the pH is lowered, however, the overall surface charge on the cells will become positive which will inhibit the approach of positively charged metal cations. It is likely that protons will then compete with metal ions for the ligands, thereby decreasing the interaction of metal ions with the algal cells.

The ions which form Class II are anionic in nature. We believe that the interaction of these ions with the algal cell is primarily electrostatic in nature. This is consistent with the fact that Class II ions do not bind at high pH where the overall algal surface charge is negative, but that they do bind at low pH where the algal surface charge will be positive.

Those metal ions in Class III are comprised of Ag^+, Hg^{+2} and $AuCl_4^-$. These metal ions, being "soft" in nature, prefer to form covalent complexes with "soft" ligands which contain the

elements of nitrogen and sulfur. The reaction of these metal ions would therefore be expected to rather pH independent.

Table I summarizes data obtained from experiments such as those shown in Figure 1. The data shows the relative affinity of the algal biomass for different metal ions under a given set of conditions. At pH 5, Ag^+, Hg^{+2}, $AuCl_4^-$ and UO_2^{+2} are most strongly bound of all metal ions tested, while Zn^{+2} and Ni^{+2} are the more weakly bound in the acetate buffer system.

Table 1. Metal Ion Binding to <u>Chlorella vulgaris</u>

TEST METAL ION	% REMOVED	INITIAL CONCENTRATION
Au(III)	100	
Ag(I)	100	1.0×10^{-4} M, pH 2-7
Hg(II)	100	
U(VI)	100	
Cu(II)	90	
Be(II)	80	1.0×10^{-4}M in 0.05 M
Al(III)	80	Sodium Acetate at pH 5.0
Pb(II)	75	
Cd(II)	60	
Ni(II)	40	
Zn(II)	40	
Pt(II)	90	1.0×10^{-4} M, pH 2.0
Cr(VI)	84	

Figure 2 shows that some metal ions compete with one another for binding sites on the algae. Figure 2A shows the pH binding profile for nine different metal ions in the absence of one another, whereas Figure 2B shows the pH binding profile for the same metal ions when they are all simultaneously present at the same concentrations. While it is clear that some of the metal ions compete with one another for algal binding sites, it is of interest to note that the bindings of Ag^+ and Al^{+3} are

relatively unaffected by each other or other metal ions. This suggests that at least two classes of binding sites exist, one with specificity for hard ions such as Al^{+3} and others with specificity for soft ions such as Ag^{+}.
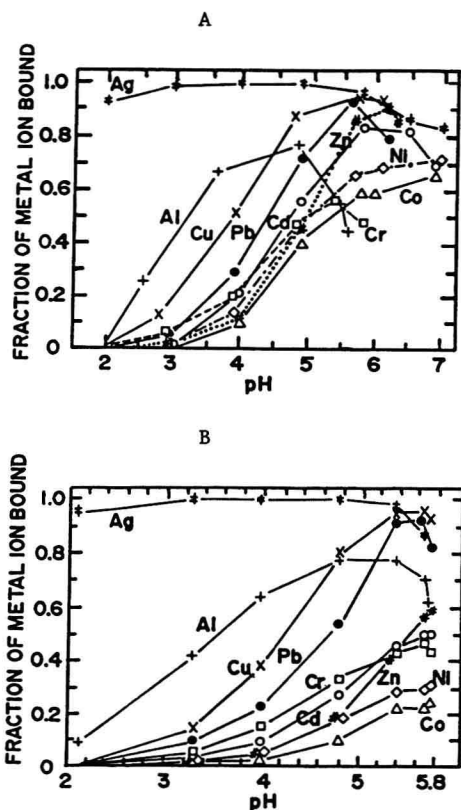

Figure 2. The Competition of Metal Ions for Binding Sites on *Chlorella vulgaris*. A. Algae (5 mg/ml) was reacted at the indicated pH values with separate solutions of each of the ions shown above at concentrations of 0.1 mM in 0.05 M acetate. After two hours the solutions were centrifuged and the supernatants were analyzed for the appropriate metal ion. The ordinate represents the fraction of metal ion removed from solution. B. This illustrates the same data as in A, except that all nine metal ions were simultaneously present during the experiment.

Initial experiments indicated that Ca^{+2} and Mg^{+2} were rather weakly bound by the algae. This suggests that the components of hard water may interfere minimally with the binding of transition metal ions to the algal system. That this is the case is shown in Figure 3 where it is seen that concentrations as high as 2000 ppm of Ca^{+2} and Mg^{+2} only inhibit the binding of 0.1 mM Cu^{+2} by about 30 percent.
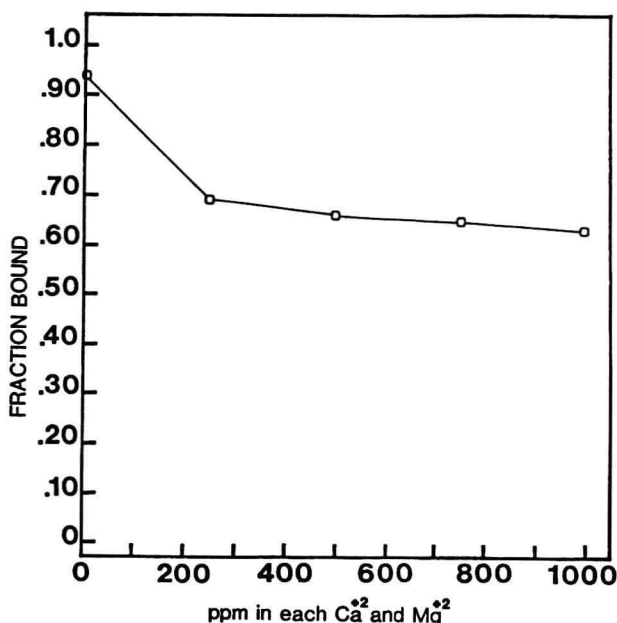

Figure 3.   The Effect of Calcium and Magnesium Ions on the Binding of Copper Ion by Chlorella vulgaris. Conditions of the experiment were identical to those described for Figure 2A.

Uranyl Ion Binding.

The uranyl ion was found to be very strongly bound by Chlorella. However, when ground waters containing UO_2^{+2} were treated with algae, it was clear that an interference was present that inhibited the binding of UO_2^{+2} (Figure 4). Thus we
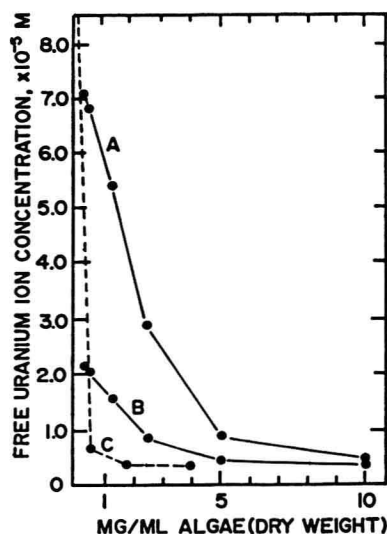
Figure 4.   The Removal of Uranium Ion from Ground Waters and
             from Solutions of 0.05 M Sodium Acetate at pH 5.0.
             Solutions A,B, and C reacted with increasing amounts
             of dried algae. After two hours the suspensions were
             centrifuged, and the free uranium concentrations in
             the supernatants were determined. A and B represent
             two different ground water samples taken from the
             Ambrosia Lake area of northern New Mexico: Each was
             at pH 7.6, and no pH adjustments were made. C
             represents a solution of 0.05 M NaOAc at pH 5
             containing an initial concentration of 0.1 mM
             uranylacetate. The results suggest the presence of
             interfering species in the ground water samples.

examined the effects of different salts on the binding of UO_2^{+2}

to <u>Chlorella</u>. It was found that sodium acetate, sodium

chloride, sodium nitrate and sodium sulfate were without effect

on the binding of UO_2^{+2}, but that sodium phosphate inhibited the

binding somewhat and sodium carbonate was inhibitory at even

very low concentrations (Figure 5). Since the uranyl ion forms

to strong complexes with carbonate, it was likely that carbonate

was effectively competing as a ligand for UO_2^{+2}. The

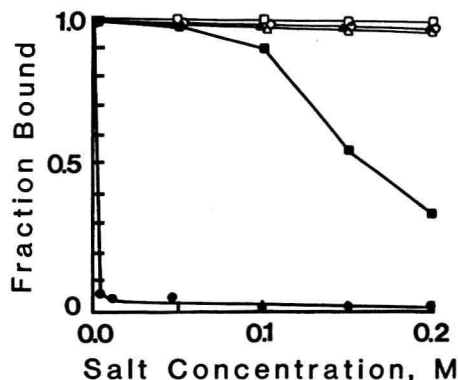interference of carbonate can be completely eliminated, however,

Figure 5.   The Effect of Salts on the Binding of Uranium (VI) to
            Chlorella vulgaris at pH 8. Algae was suspended at
            1.5 mg/ml in solutions which contained 0.05 M sodium
            acetate at pH 8, 0.1 mM uranium (VI) acetate, and a
            different salt concentration. The salt solutions
            used were sodium acetate (□), sodium bicarbonate (●),
            sodium chloride (o), sodium hydrogen phosphate (●),
            sodium nitrate (▲), and sodium sulfate (△).

by careful control of pH. Figure 6 shows that the binding of

UO_2^{+2} to Chlorella is not detectable in laboratory samples or

industrial mill-water samples which contain carbonate/

bicarbonate near pH 8. However, as soon as the pH of these

solutions is decreased to pH 5, complete binding occurs. This

can be explained by the fact that as the pH is lowered,

carbonate and bicarbonate are protonated which leads to CO_2

being lost from the solution, and the carbonate interference is

eliminated.[20]

     The fact that carbonate was found to interfere strongly

with UO_2^{+2} binding suggests that carbonate might be used to

strip bound UO_2^{+2} from from algal cells. Figure 7 shows an

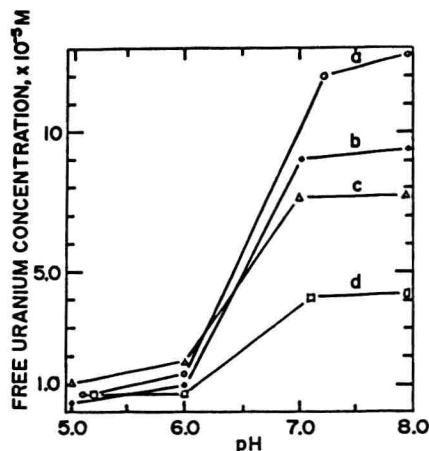experiment in which a 1.0 mM solution of UO_2^{+2} was passed

Figure 6. The Effect of pH on the Removal of Uranium Ion by Algae from Mill Waters and Sodium Bicarbonate Solutions. Algae suspensions in mine waters (curves a,c, and d) and 0.05 M sodium bicarbonate (curve b) were adjusted to the indicated pH values (original pH was 8). The suspensions were allowed to react for 2 hours, at which time they were centrifuged, and the amount of uranium ion remaining in the supernatant was determined. It is apparent that sodium bicarbonate strongly inhibits the binding of uranium ion to algae above pH 5 or 6. Algae-free control samples showed that pH adjustment alone did not result in any precipitation of uranium ion.

through a column containing <u>Chlorella</u> <u>vulgaris</u> immobilized in polyacrylamide. After passing 80 ml of the uranyl solution through the column and after extensive washing, no UO_2^{+2} was detected in the effluent. The bound UO_2^{+2} was then quantitatively recovered upon elution of the column with 0.05M $NaHCO_3$ at pH 8.0.

<u>Gold Ion Binding</u>.

Although the data in Figure 1 indicates that gold as $AuCl_4^-$ is bound independently of pH, the same is not true of all