Adsorption of metal cations by hydrous aluminium(III) or iron(III) hydroxide precipitates: enhancement by EDTA and related chelate molecules†

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Stoichiometrically equivalent concentrations of ethylenediaminetetraacetate, EDTA, and of related chelating anions increase the adsorption of *ca.* millimolar concentrations heavy metal aqua-ions on amorphous precipitates of aluminium(III) or iron(III) hydroxide and, although higher concentrations decrease the adsorption, poly-EDTA, a polyelectrolyte containing EDTA functional groups, shows no such decrease.

Inorganic coagulants, such as aluminium(III) or iron(III) salts, are widely used both for cleaning potable water and also for treating a variety of aqueous effluents.[1] The gelatinous metal hydroxide or floc is also used in the treatment of effluents containing heavy metal cations since these are adsorbed[2] by the floc even though they are generally soluble at the pH used. The method is thought to be less successful in the presence of coordinating ligands since these often form soluble metal complexes which are only adsorbed by the floc at pH values[3,4] below those customarily used in water treatment by, for instance, hydrous ferric oxide.[1] However, much of the work in this area is concerned with metal adsorption in sediment or soil so that hydrated aluminium or iron oxides[5] are the absorbents usually studied. Although solutions of EDTA are believed to strip metal cations from soils[6] where they are supposed to be bound by aluminium(III) or iron(III) oxides, EDTA at concentrations comparable to those of the adsorbed metal ions, can increase their adsorption at pH values below 7 through electrostatic binding of the anionic complexes.[5] In this work we have examined the effect of EDTA on heavy metal adsorption during the precipitation of amorphous aluminium or iron hydroxide under conditions typical of those used during effluent treatment. We find that copper, nickel and cadmium show an enhanced cationic adsorption on aluminium hydroxide at pH 7, both separately and when mixed in the same solution. Enhanced adsorption at pH 7 has only been found on an iron(III) floc in the single case of mercury(II). The effect has been studied in more detail for cadmium on aluminium(III) but the similar trends observed in all cases suggest that one theoretical explanation is common to all.

The adsorption experiments were carried out by mixing reagent solutions at a pH of *ca.* 3 and then adjusting the pH to 7 sufficiently slowly to ensure that the final value during processing was 7.000 ± 0.005. The floc and supernatant solution were separated by centrifuging, the floc was redissolved in concentrated nitric acid and then analysed by ICP-AE. A correction was applied in all cases to allow for the adsorbate ions present in the solution which was trapped within the floc gel phase. In some experiments the EDTA present in each phase was estimated spectroscopically at 460 nm by complexation at pH 3 with zirconium(III).

The approach to equilibrium is rapid if all the components are present prior to the adjustment of the pH to 7 but it is slower if, for instance, the floc is formed prior to the addition of EDTA or cadmium. These results resemble the leaching experiments reported[7] previously with a range of hydrous metal oxides. A typical experiment is shown in Fig. 1 for cadmium(II) adsorbed by a floc of aluminium(III). The fraction of cadmium adsorbed decreases progressively with increasing concentration of EDTA as would be expected if the adsorbed ions were being removed from the floc because of the formation of unadsorbed EDTA–metal complexes. However the extrapolated adsorption at zero EDTA is 100% whereas the measured value is 40%. This apparent discontinuity is explained when the experiments are extended to much lower EDTA concentrations, Fig. 2. It is now obvious that the effects of trace amounts of EDTA is to increase the fraction of the metals adsorbed by the floc. The adsorption of the Cd^{2+} in the presence of a stoichiometric equivalent of EDTA increases as the pH rises showing that it occurs at a cationic site despite the anionic character of dissolved $[Cd(edta)]^{2-}$.

The concentration of aluminium found in solution increases with that of EDTA and may be calculated on the basis of the accepted values of the solubility product of aluminium hydroxide and the binding constant of the aluminium–EDTA complex,[8] as shown in Fig. 1.

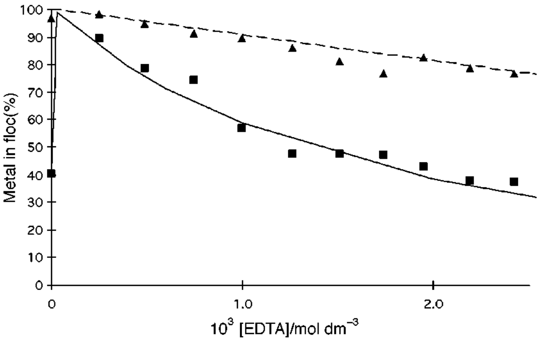

Fig. 1 Effect of EDTA at pH 7, 9.3 mM Al^{3+} and 22.2 μM Cd^{2+}: (■) % Cd(exptl.), (▲) % Al(exptl.), (——) % Cd(calc.), (- - - -) % Al(calc.).

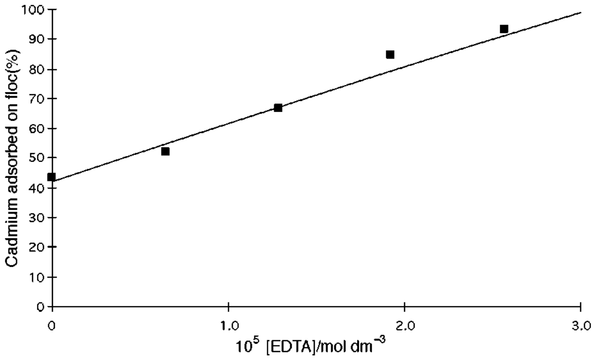

Fig. 2 Effect of low concentrations of EDTA, 12.3 mM Al^{3+} and 29.4 μM Cd^{2+}: (■) % Cd(exptl.), (——) % Cd(calc.).

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It has been found that changes in the EDTA structure do not prevent enhanced metal ion adsorption. Cyclohexylaminetetraacetate and nitrilotriacetate will also promote cadmium retention in aluminium floc although they are much less effective. The enhanced adsorption of cadmium also occurs when the EDTA is in the form of a polyelectrolyte, poly-EDTA, made by the condensation of polyallylamine and ethylenediaminetetraacetic dianhydride.[9] However, although the poly-EDTA enhances adsorption in the same way as does EDTA, the decline in adsorption at higher concentrations shown in Fig. 1 does not occur and the aluminium floc dissolves to a much smaller extent, by 1–2%.

The structure of the species present in the gel phase and in solution have been investigated using EXAFS which reveals the short range order within an amorphous precipitate as well as the corresponding order in the dissolved complexes. The results for cadmium adsorbed on aluminium floc show that the adsorbed metal in the absence of EDTA is identical with the aqua-cation whereas in the presence of EDTA it resembles the dissolved EDTA complex in solution. The compound adsorbed in the gel phase appears to be a six-co-ordinate complex in which the nitrogen or oxygen atoms are present at 0.24 nm from the metal atom. These results suggest that Cd^{2+},edta,Al^{3+} complexation contributes to the binding of cadmium on cationic sites but with only a slight distortion of the normal Cd^{2+},edta complexation found in solution.

The enhanced adsorption and its eventual inhibition by EDTA can be modelled by an equilibrium system provided a suitable adsorption inhibition step is postulated. The adsorption of metal aqua-ions by both aluminium and iron flocs is generally supposed to take place by binding at metal cation exchange sites. Corresponding anion binding sites are also supposed to exist to explain the removal of anions by the same floc.[5] The eventual stripping of the adsorbed metal from the floc is usually attributed to the formation of soluble metal chelates by EDTA. However if a cadmium–edta species is responsible for the enhanced binding, this no longer explains the final desorption stage. The EDTA cannot be operating by combining with the floc adsorption sites since the concentration of the chelate is more than a hundred-fold less than that of the aluminium atoms present. The simplest equilibrium step producing a satisfactory model appears to be the formation of a soluble polynuclear chelate containing both an adsorbent and an adsorbate atom together with at least two EDTA molecules. There is considerable evidence that the formation of polynuclear species is promoted by the presence of organic ligands and solid aluminium hydroxide.[10] Although EDTA complexes of this type have not previously been suggested, polynuclear carboxylate complexes are well known to exist.[11] Equilibria (1)–(7) below reproduce the essential features of our observations and the data in Figs. 1 and 2.

$$Al^{3+} + 3OH^{-} \rightleftharpoons G_{gel} \tag{1}$$

$$Al^{3+} + edta^{4-} \rightleftharpoons [Al^{3+}(edta^{4-})]^{-} \tag{2}$$

$$Cd^{2+} + edta^{4-} \rightleftharpoons [Cd^{2+}(edta^{4-})]^{2-} \tag{3}$$

$$H_2O \rightleftharpoons OH^{-} + H^{+} \tag{4}$$

$$G_{gel} + Cd^{2+} \rightleftharpoons [Cd^{2+}(G)]_{gel} + xH^{+} \tag{5}$$

$$Cd^{2+} + edta^{4-} + G_{gel} \rightleftharpoons [Cd^{2+}(edta^{4-})(G)]_{gel} + yH^{+} \tag{6}$$

$$[Cd^{2+}(edta^{4-})(G)]_{gel} + edta^{4-} \rightleftharpoons [Cd^{2+}(edta^{4-})Al^{3+}(edta^{4-})]^{3-} \tag{7}$$

Gelatinous hydrous aluminium oxide is denoted by G_{gel} and all species subscripted by 'gel' are adsorbed in the floc. The number of adsorbent sites was always greatly in excess of the number of adsorbed species so that the number of sites per gm atom of aluminium could be taken to be constant. The calculated concentration of undissolved aluminium, $[Al^{3+}]_{floc,}$ was therefore assumed in eqns. (5) and (6) to be linearly related by the constant α to the concentration of free adsorption sites per unit volume of solution, Γ,

$$\Gamma = \alpha[Al^{3+}]_{floc}$$

The values for the ionic product of water, the solubility product of aluminium hydroxide and the association constants of EDTA with aluminium and cadmium were taken from the literature[8] and the constants $\alpha K_5/[H^+]^x$, $\alpha K_6/[H^+]^y$ and K_7 were fitted. There was no need to determine x or y since the pH was constant at 7. The theoretical curves in Figs. 1 and 2 were calculated by the iterative solution of the set of equations derived from equilibria (1)–(7). The agreement of experiment and theory shows that the explanation is consistent with observation although further investigation is necessary to establish the structure of the postulated polynuclear soluble species. The same model may also be used successfully to reproduce the effects of pH and the EDTA enhanced metal ion adsorption in other systems.

The fact that enhanced binding may be produced by a chelating polymer without the undesirable side-effects of aluminium and adsorbate solution eventually produced by EDTA suggests that useful new polyelectrolytes may be synthesised which could enhance the flocculative treatment of heavy metal contaminated aqueous wastes.

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