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The effect of co-precipitation on cadmium(II) adsorption on hydrous aluminium(III) hydroxide in the presence of a range of chelates

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The adsorption of cadmium(II) on freshly precipitated aluminium(III) hydroxide in the presence of a range of chelates has been investigated. By precipitating the metal, chelate and adsorbent together it is possible to change the pH variation of the metal-complex adsorption from anionic, "ligand-like", binding to cationic binding. This is a general phenomenon and is explained by the formation of a ternary Al–O–Cd–L surface species. As a consequence of the preparation method, the pH edge is found to shift to lower pH values in the presence of the chelate which gives rise to an apparent increase in adsorption of Cd^{2+}. This increase is, in general, most pronounced at $[\text{chelate}]/[\text{metal}] > 1$. Computer modelling shows that the observed trends result from the competition between Al–O–Cd–L and Al–L for the available aluminium(III) binding sites. The enhanced adsorption in the presence of phenylenediaminetetraacetate is anomalous since it is observed at a $[\text{chelate}]/[\text{metal}] \approx 0.1$ and cannot be interpreted by the simple competition model.

Introduction

Inorganic coagulants, such as aluminium (III), are widely used for cleaning potable water and a variety of aqueous effluents.[1] The process depends on adding the metal salt to the water under treatment and adjusting the pH of the mixture to the range within which the amorphous metal hydroxide is precipitated. The resulting 'floc' is removed carrying with it pollutants such as micro-organisms, particulate materials, inorganic species and organic substances. They are removed by particle entrapment, colloid destabilisation and in the case of heavy metal cations, adsorption of dissolved compounds.[2]

This paper describes the results from the adsorption of Cd^{2+} on hydrous aluminium hydroxide in the presence of a variety of chelates. Understanding the effect of chelates and organic matter on the speciation of metals in solution in the presence of hydroxides is important and has been studied extensively.[3] The adsorption of a variety of metals such as Cu^{2+}, Zn^{2+}, Pb^{2+} as well as Cd^{2+} on both iron and aluminium based systems has been studied in the presence of small chelates, such as EDTA, as well as polymeric matter such as humic and fulvic acids, for example.[4–8] The presence of chelates can be problematic in water treatment. For example, precipitation of heavy metals which form insoluble hydroxides and carbonates is also used to treat waste water; however the presence of chelates which complex the metal prevent efficient and reliable removal of the pollutant.[9]

The present study is part of a continuing research project aimed at improving the efficiency of flocculation in removing heavy metals from wastewater in the presence of chelates. This research has therefore concentrated on freshly precipitated hydrous oxides. In many of the previous studies, especially those involving aluminium, either aged or dried samples or rehydrated aluminium oxide were studied which behave differently from freshly precipitated systems. For example, the adsorption of copper, nickel and cadmium was enhanced by the presence of EDTA at pH 7[10,11] with freshly precipitated aluminium hydroxide but no comparable effect was reported in similar experiments with γ-alumina.[12,13] Cadmium in an equimolar mixture with EDTA, moreover, was more strongly adsorbed as the pH[10,11] increased although the trend reported previously for γ-alumina was exactly the reverse.[14]

In this paper, we show that the changes observed in the presence of EDTA are common to a wide range of EDTA like chelates. The model proposed[11] to explain the EDTA adsorption, is shown to be capable of predicting the behaviour of all the systems studied apart from PhDTA. Fig. 1 shows the structures and abbreviations for all chelates used in this study.

Experimental

Analytical methods

Metal ion concentrations were measured using a Perkin Elmer Atomic Emission Spectrometer Plasma 400. Solution pH was measured by a Metrohm 713 pH meter, calibrated before each set of observations using standard NBS buffers at pH 4, 7 and 10. The reported hydrogen ion concentrations were calculated from pH measurements using the standard NBS activity correction procedure.[15] The effect of varying liquid junction potentials[16] calculated from the Henderson equation was negligible.

Reagents

Sodium hydroxide, disodium ethylenediaminetetraacetate dihydrate (EDTA), *N*,*N*,*N*′,*N*′-phenylenediaminetetraacetic acid (PhDTA), *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid monohydrate (CDTA), 1,3-diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetic acid (PDTA), trisodium [*S*,*S*]-ethylenediamine-*N*,*N*′-disuccinate (EDDS), nitrilotriacetic acid (NTA), aluminium nitrate nonahydrate, zirconyl chloride octahydrate, and nitric acid were Analar quality. Cadmium nitrate tetrahydrate was GP quality. Distilled deionised 18.2 MΩ water was used to prepare the stock solutions.

1,6-Diaminohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid (HDTA) was synthesised using the method developed by Ogino *et al.*[17] Monochloroacetic acid (17 g, 0.18 mol) was dissolved in water

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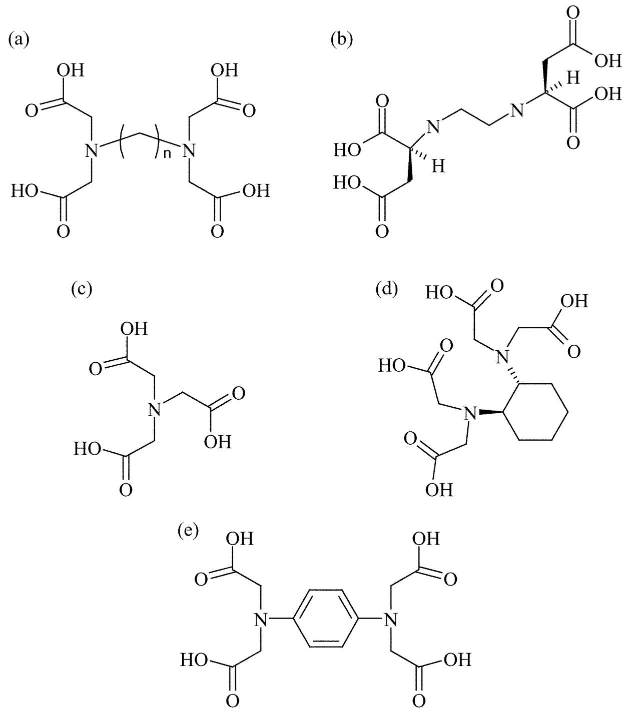

Fig. 1 Structures of (a) EDTA ($n = 2$); PDTA ($n = 3$); HDTA ($n = 6$), (b) EDDS, (c) NTA, (d) CDTA and (e) PhDTA.

(50 cm^3) to which sodium hydroxide (14.4 g, 0.36 mol), dissolved in the minimum amount of water, was added drop-wise, with stirring, at 10 °C. This was followed by the addition of hexamethylenediamine (3.5 g, 0.03 mol). The resulting solution was heated at 100 °C for 1 h and was left to stand overnight. The pH of the cooled solution was adjusted to 2.3 with 36% concentrated hydrochloric acid and was rotary evaporated giving a white powder containing sodium chloride. The mixture was washed three times with distilled deionised 18.2 MΩ water to remove the sodium chloride and the solid recrystallised from hot water, resulting in the hydrate. Recrystallisation was repeated twice. A yield of 4.66 g, 44.6%, was obtained. NMR δ^1H/ppm (D$_2$O) 1.25 (4H, s), 1.45 (4H, s), 2.55 (4H, t), 3.20 (8H, s), CHN found: C, 47.63; H, 6.79; N, 7.76%. Calc.: C, 48.28; H, 6.90; N, 8.05%. ν(IR)/cm^{-1}: 1300–1375 (–CH$_2$– bend), 1691 (C=O), 3000–3150 (C–H stretch), 3450 (OH).

Floc preparation by co-precipitation

The floc suspensions were prepared in 50 cm^3 beakers using stock solutions at ambient temperature, 22 ± 1 °C, measured by the pH meter platinum resistance thermometer. A mixture containing various concentrations of aluminium, cadmium and chelate, 30 cm^3 in total volume, was magnetically stirred while the pH was adjusted to within ±0.005 pH units of the nominal value using 5 M sodium hydroxide and 0.1 M nitric acid as required. The pH was adjusted over various time periods, up to 2 days, to ensure that equilibrium had been achieved. It should be noted that after the initial rapid changes of pH within the first 10 min, the maximum pH change observed was only −0.1 pH units. Following pH adjustment, the solution was decanted into a 50 cm^3 polyethylene tube and centrifuged for 5 min at 2500 rpm (equivalent to 1120 g). The supernatant solution was decanted and the precipitate was dissolved in 1 cm^3 68% nitric acid and made up to 50 cm^3 total volume. In computing the amounts of aluminium and cadmium in the precipitate, allowance was made for the supernatant solution, which was unavoidably transferred with the solid phase. Centrifugation was not found to be an efficient process in fully removing the precipitate from the supernatant solution at pH values below 6. Therefore, in order to be able to analyse both the precipitate and the supernatant without the results for the latter being compromised by the presence of precipitate, filtration using 0.45 μm Millipore PVDF membrane was employed. Comparison of the two separation techniques using higher pH values showed little difference in the results obtained. The volumes for each floc formed were measured by dissolving the floc pellet in a known volume of 68% nitric acid and measuring the difference in volume between the dissolved pellet and the added acid. For all experiments the ionic strength was 0.037 M.

Modelling

The computer model used to simulate the adsorption reactions was developed using Microsoft Excel and copies are available from the principal author on request. Details of the calculations and the procedures used have been published previously[11] and are further discussed below.

Results and discussion

Kinetics of adsorption

The results reported in this paper have all been obtained under conditions broadly described as co-precipitation although, strictly speaking, the mechanism is that of floc precipitation followed by metal ion and chelate adsorption. The quasi-equilibrium is reached rapidly in the 5–10 min before the first observation can be made and no significant variation occurs thereafter. This is shown in detail for cadmium with both EDTA and EDDS in Fig. 2. Fig. 2 shows that the degree of adsorption was constant over a period of 50 h following the initial precipitation at either pH 6.5 or 7.0.

Equilibrium simulation

The data are interpreted by the following set of balanced reactions:

$$\mathrm{Al^{3+} + edta^{4-} \rightleftharpoons Al(edta)^{-}} \tag{1}$$

$$\mathrm{Cd^{2+} + edta^{4-} \rightleftharpoons Cd(edta)^{2-}} \tag{2}$$

$$\mathrm{G_{gel} + Cd^{2+} \rightleftharpoons Cd^{2+}, G_{gel} + xH^{+}} \tag{3}$$

$$\mathrm{Cd^{2+} + edta^{4-} + G_{gel} \rightleftharpoons Cd^{2+}, edta^{4-}, G_{gel} + yH^{+}} \tag{4}$$

$$\mathrm{G_{gel} + edta^{4-} \rightleftharpoons edta^{4-}, G_{gel}} \tag{5}$$

$$\mathrm{Al^{3+} + 3H_2O \rightleftharpoons G_{gel} + 3H^{+}} \tag{6}$$

$$\mathrm{G_{gel} + H_2O \rightleftharpoons Al(OH)_4{}^{-} + H^{+}} \tag{7}$$

$$\mathrm{Al(edta)^{-} + H_2O \rightleftharpoons Al(OH)(edta)^{2-} + H^{+}} \tag{8}$$

$$\mathrm{Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3(aq) + 3H^{+}} \tag{9}$$

$$\mathrm{Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2{}^{+} + 2H^{+}} \tag{10}$$

$$\mathrm{Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^{+}} \tag{11}$$

in which the symbol G$_{\mathrm{gel}}$ represents the hydrous floc surface free of adsorbed edta^{4-} or Cd^{2+}. Throughout the text, the equilibrium constants for each reaction (x) are denoted by K$_x$. Reaction (8) was not originally included[11] in the equilibrium set because of its supposed trivial contribution to the adsorption equilibrium. Subsequently it was realised that Al(OH)(edta)$^{2-}$ did have a marked effect on the absolute equilibrium concentrations and consequently on the absolute value of the fitted constants K_3, K_4 and K_5. The inclusion of reaction (8), however, does not affect the overall fitting of the observed trends to the proposed model but only the fitting parameters required.

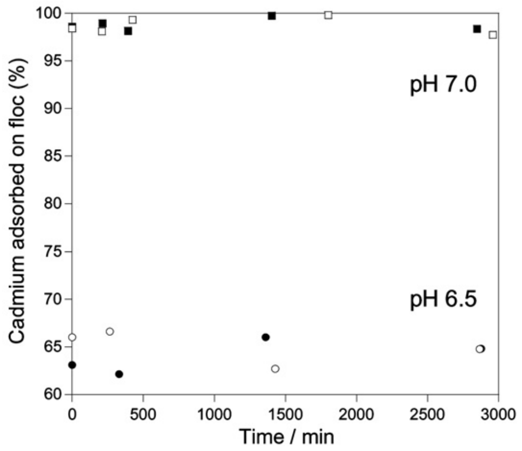

Fig. 2 Variation of %Cd contained in the floc adsorbed with time from a co-precipitated solution at pH 6.5 (circles) and pH 7.0 (squares) containing 333 ppm Al, 3.33 ppm Cd (12.3 mM Al^{3+} and 29.7 μM Cd^{2+}) with 0.067 mM EDDS (unfilled symbols) and 0.033 mM EDTA (filled symbols).

The species included are only those which could play a rôle in the enhanced adsorption of cadmium. A full equilibrium set would include many other species which never attain significant concentration and which only confuse the interpretation of the observed adsorption.

In the case of EDTA, it is necessary to make allowance for the effect of the various deprotonated forms in calculating the concentration of $edta^{4-}$ even though the other forms do not participate in the cadmium(II) or aluminium(III) binding. The ion $edta^{4-}$, which is the dominant complexing form of EDTA, is the only EDTA species to appear in the simulation but the effect of the other EDTA species is allowed for by the use of conditional constants[18] for K_1, K_2 and K_5. A full allowance is made for H_4edta, H_3edta^-, H_2edta^{2-}, $Hedta^{3-}$, as well as the ion-paired species derived from the presence of the sodium counter-ions[19] and a minor contribution[20] due to the formation of $Cd(NO_3)^+$. Each conditional constant is calculated using α,

$$\alpha = [edta^{4-}]/([edta^{4-}] + [Hedta^{3-}] + [H_2edta^{2-}] + [H_3edta^-] + [H_4edta])$$

$$K_{conditional} = \alpha K$$

where K is the thermodynamic binding constant for a reaction involving $edta^{4-}$.

There are many other complexes which have been have been suggested for aluminium(III) and cadmium(II) under acid or alkaline conditions. At low pH there is a range of protonated EDTA complex ions which have been invoked to explain equilibrium measurements for cadmium[21] and for aluminium.[22] However, within the pH range from 5–10, their concentration appears to be negligible. The ion $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$ should apparently be formed[23] within this pH range but it could not be detected by ^{27}Al NMR spectroscopy and has been omitted.[11] It is known that it is formed only slowly and under favourable conditions.

The concentration of the aluminium species in solution is controlled by the solubility of the floc, equilibrium (6) and its speciation by equilibria (1), (7)–(11).[24,25] At a pH below 6, the aquo aluminium ion and the hydroxyaluminium ions $Al(OH)^{2+}$ and $Al(OH)_2{}^+$ dominate the speciation, whereas the $Al(OH)_3$ (aq) species is never present in significant concentrations at any pH between 5 and 10. Above pH 6.5 the $Al(OH_4)^-$ ion is the predominant soluble aluminium species present.[24] The aquo cadmium ion is known[26] to deprotonate significantly to form $Cd(OH)^+$ and $Cd(OH)_2$ above pH 9 but the dissolved uncomplexed cadmium concentration is then always negligible so that $Cd(OH)^+$ and $Cd(OH)_2$ need not be included.

Equilibria (1), (2) and (6) have been studied previously over a wide range of temperatures and ionic strengths[11] and these results have been formulated for this study using the techniques developed by Daniele *et al.*[19] in order that the constants may be calculated for virtually any temperature and ionic strength. Reactions (7), (9)–(11)[25] and (8)[27] are less thoroughly documented and corrected only for the effects of ionic strength using the Davies equation. The experiments modelled in this paper have been performed at 22 °C and an ionic strength of 0.037 M so that the fitted constants for equilibria (3)–(5) are single values appropriate for that temperature and ionic strength. The constants for reactions (1),[28] (2)[29] and for the acid dissociations[30] of EDDS used in modelling with the latter are generally less well established than those for EDTA. They have been corrected for ionic strength variation only.[19]

The simultaneous equations which may be derived[11] for the ion concentrations in the equilibria (1)–(11) are solved digitally by starting from plausible estimates of the unknown concentrations and iterating using the procedures found in Microsoft Excel until the final and penultimate values agree. Generally ten or twenty cycles are sufficient for the results to converge.

The modelling studies broadly indicate that the trends in the enhanced adsorption depend on the competition between reactions (4) and (5). The numerical values of the constants K_4 and K_5 are altered by changes in the postulated solution equilibria but the final agreement of model and observation is unaffected.

Cadmium adsorption in the presence of EDTA

Fig. 3 shows the variation of adsorbed Cd^{2+} in the presence and absence of EDTA with pH. Both sets of data show an increase in adsorption with pH but in the presence of EDTA the pH edge has been shifted from 7.0 to 6.0. The shift in the pH edge leads to an apparent enhanced adsorption at pH 7.0 in the presence of EDTA over the system where the chelate is not present. The lines in Fig. 3 show the predicted trend from the model simulated using eqns. (1)–(11) above. Fig. 4 indicates how the concentration of the species contained within the model vary with pH for the co-precipitation of Cd^{2+} and Al^{3+} in the presence of EDTA.

The variation of adsorbed Cd^{2+} with increasing concentrations of EDTA is shown in Fig. 5. As the concentration of EDTA increases, a sharp rise in Cd^{2+} adsorption is observed which reaches a maximum at 0.033 mM. At this point, the

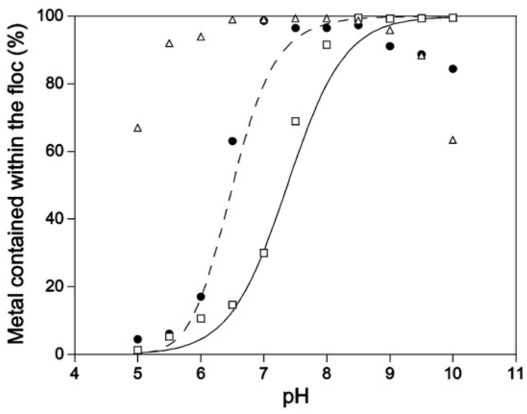

Fig. 3 Variation of %Cd adsorbed with increasing pH from a co-precipitated solution containing 333 ppm Al, 3.33 ppm Cd (12.3 mM Al^{3+} and 29.7 μM Cd^{2+}) and 0.033 mM EDTA (●, dashed line) and distilled water (□, solid line). Lines indicate predicted trend from the model and the % Al (△) within the floc is shown for the solution containing EDTA.

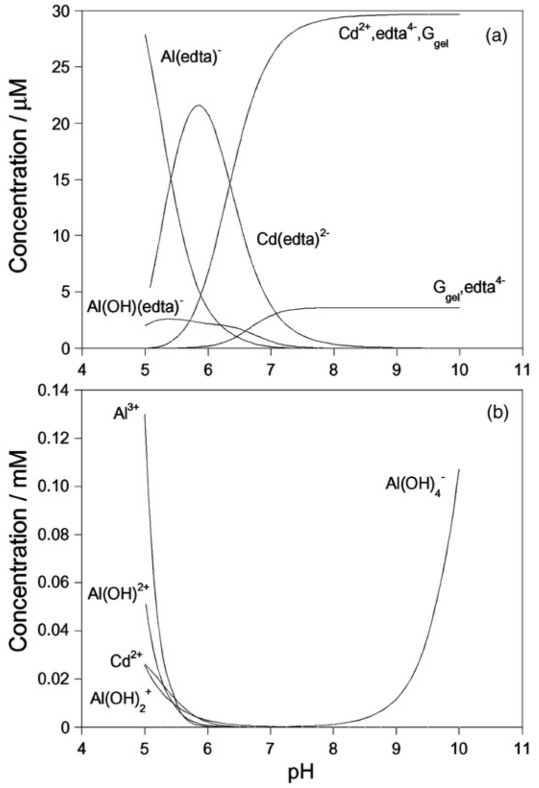

Fig. 4 Variation in the concentration of the dominant (a) complexed EDTA and (b) non-EDTA species present during co-precipitation of a solution containing 333 ppm Al, 3.33 ppm Cd (12.3 mM Al^{3+} and 29.7 µM Cd^{2+}) and 0.033 mM EDTA predicted from the model. The $Al(OH)_4^-$ concentration is divided by 50.

EDTA and cadmium present are approximately equimolar. Further increases in EDTA result in a drop in adsorbed Cd^{2+} with a concomitant decrease in the Al^{3+} contained within the precipitate.

Increasing metal adsorption in the presence of a chelate with increasing pH is unusual. Commonly in the presence of chelates, the opposite variation is observed,[14] *i.e.* a decrease in adsorption with increasing pH, typifying metal–EDTA *anionic*, "ligand-like", adsorption. The profile observed in Fig. 5 indicates cationic adsorption normally associated with metal adsorption in the absence of a chelate. This change in pH profile is a direct consequence of the preparation method. Unlike in the majority of studies, we mixed the Cd^{2+}, Al^{3+} and EDTA prior to pH adjustment so that they were finally *co-precipitated*, *i.e.* the hydroxide is formed in the presence of the Cd^{2+} and EDTA. If the hydroxide is formed prior to adsorption, the adsorption of Cd^{2+} decreases at pH values above 6.5, in the presence of EDTA which is consistent with the binding of an anionic Cd–EDTA complex and is in agreement with many previous studies.[12,14] The decrease in adsorption with decreasing pH cannot be explained *via* the dissolution of the floc. For example, when the Cd^{2+}, Al^{3+} and EDTA are coprecipitated, there is a substantial decrease in the adsorbed Cd^{2+} contained within the hydrous floc at pH 6.0, from 100% to 17%, yet less than 6% Al^{3+} dissolution is observed, as shown in Fig. 3. It should be noted that it is *only below* pH 5.5 that dissolution of Al^{3+} becomes significant and this is independent of the order in which the reagents are precipitated or whether chelate is present.[31]

In the absence of EDTA, the metal binds as uncomplexed metal to the floc oxide surface, eqn. (3), and shows typical cationic adsorption characteristics associated with the change in surface charge of the floc surface with pH. With increasing concentrations of EDTA, the rise in cadmium adsorption is not due to the trapping of a cadmium ion within an EDTA molecule, which is then bound to the aluminium ions in the precipitate as an anion and would show a ligand like binding pH curve, but rather to the formation of a distinct ternary complex, as shown in eqn. (4), resulting in the opposite (cationic) pH profile, as described above. This type of reaction may perhaps depend on the reactivity of small aluminium(III) aggregates formed during precipitation as opposed to the final stable floc surface.

Cadmium adsorption in the presence of EDDS

Cationic-like binding of Cd^{2+} in the presence of a chelate is a general phenomenon when Al^{3+}, Cd^{2+} and chelate are co-precipitated. Fig. 6 shows the variation of adsorbed Cd^{2+} on aluminium hydroxide with pH in the presence of EDDS. EDDS is of particular interest since it is readily biodegradable both as the free ligand and when complexed with some heavy metals, for example Cd^{2+}.[32] As with EDTA, Cd^{2+} adsorption increases with increasing pH and the pH edge is shifted from approximately 7.0, for the metal alone, to 6.0, when EDDS is present. It should be noted that the pH variation of the Al^{3+} contained within the floc is similar whether co-precipitation occurs in the presence of EDDS or EDTA.

Fig. 7 shows the variation of adsorbed Cd^{2+} with increasing concentration of EDDS. As with EDTA, a rapid increase in adsorption is observed. With EDDS, the limit is reached at

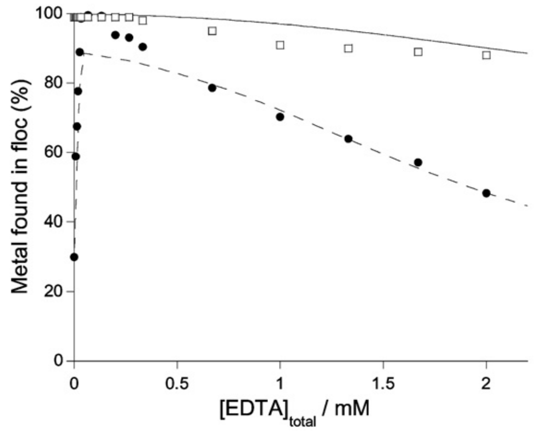

Fig. 5 Variation of %Al (□, solid line) and %Cd (●, dashed line) contained in the floc with increasing EDTA concentration formed from a solution adjusted to pH 7.0 containing 333 ppm Al and 3.33 ppm Cd (12.3 mM Al^{3+} and 29.7 µM Cd^{2+}) under co-precipitated conditions. Lines indicate predicted trend from the model.

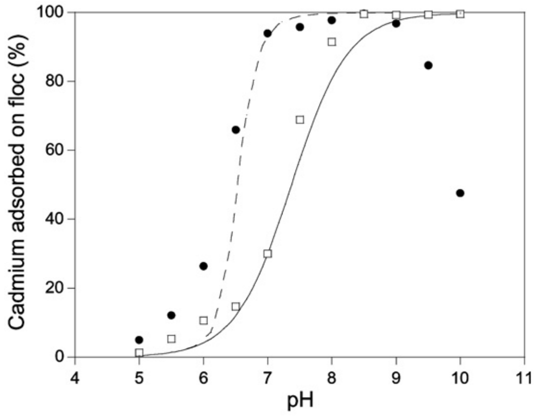

Fig. 6 Variation of %Cd adsorbed with increasing pH from a co-precipitated solution containing 333 ppm Al, 3.33 ppm Cd (12.3 mM Al^{3+} and 29.7 µM Cd^{2+}) and 0.067 mM EDDS (●, dashed line) and distilled water (□, solid line). Lines indicate predicted trend from the model.

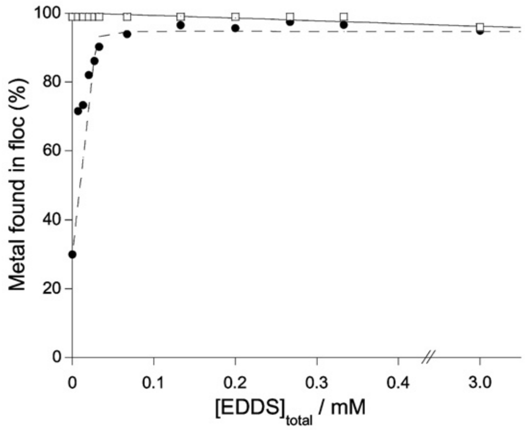

Fig. 7 Variation of %Al (□, solid line) and %Cd (●, dashed line) contained in the floc with increasing EDDS concentration formed from a solution adjusted to pH 7.0 containing 333 ppm Al and 3.33 ppm Cd (12.3 mM Al^{3+} and 29.7 μM Cd^{2+}) under co-precipitated conditions. Lines indicate predicted trend from the model.

0.07 mM, which corresponds to a chelate concentration twice that of the cadmium in the system. Unlike the case of EDTA, further increases in chelate concentration result in very little decrease in the adsorbed cadmium, even when the chelate concentration is 3.3 mM, *i.e.* one hundred-fold more concentrated than the cadmium. Compared with EDTA, adsorption in the presence of EDDS results in little reduction in the Al^{3+} contained in the floc. At pH 7.0, more than 95% Al^{3+} was retained within the precipitate over all EDDS concentrations studied.

The model equilibria (1)–(11), have been used to fit the variation of cadmium adsorption on co-precipitation as shown in Figs. 3 and 5. The results for Cd^{2+} co-precipitated with Al^{3+} and EDDS are also fitted well by this model. In Figs. 5 and 6, the lines show the simulated data. Table 1 summarises the constants for each species used to model the experimental data.

As described above, EDDS increases the adsorption of Cd^{2+} but less effectively than does EDTA at the same concentration. The model predicts this simply as a consequence of the very strong affinity of the gel surface for EDTA compared with EDDS.

In order to model the retention of Cd^{2+} on the floc successfully at high chelate concentrations, it is necessary to reduce the adsorption coefficient of the chelate on the floc. This would not be surprising in view of the structure of EDDS compared with EDTA. It has been postulated that chelates bind to hydrous flocs using hydrogen bonding.[6,33] In the case of EDDS, the carboxylic acid groups are closer than in EDTA, so that an intramolecular hydrogen bond could form a stable six membered ring. This may explain the reduction in chelate adsorption predicted by the model while the decreased bite of the chelate explains the reduced stability of the dissolved metal complexes.

The decrease in Cd^{2+} adsorption at high EDTA and EDDS concentrations cannot simply be explained by dissolution of the precipitate. The decrease in adsorbed Cd^{2+} is too large given the small decrease in hydroxide present. Although this effect contributes, we believe the major effect is due to a combination of the strong adsorption of the chelate on the floc, resulting in site blocking, and the chelate stripping the metal from the floc. In the case of EDDS, such a decrease is not observed mainly due to the much lower complexation constant for Cd^{2+} compared with EDTA. This is easily seen if eqns. (2), (4) and (5) are combined:

$$Cd^{2+}, L^{4-}, G_{gel} + L^{4-} + yH^+ \leftrightharpoons Cd^{2+}, L^{4-} + L^{4-}, G_{gel} \quad (12)$$

$$\log K_{12} = \log K_2 + \log K_5 - \log K_4$$

For EDTA, $\log K_{12}$ is 17.65 whereas for EDDS it is less than 5.72. EDDS has a much lower ability to strip the floc of the Cd^{2+} than does EDTA and hence the balance remains in favour of the adsorbed Cd^{2+}–EDDS complex rather than that in solution, even at relatively high chelate concentrations. Site blocking is a significant but secondary effect to chelate stripping and it only affects the metal adsorption at relatively low chelate concentrations before the onset of surface saturation. For example, the model shows that above 1 mM EDTA there is little variation in the amount of adsorbed chelate since the floc surface is close to saturation. Below 1 mM increased chelate adsorption mirrors the drop in metal adsorbed. More variation is observed for EDDS, however, because the floc surface is more unsaturated due to the much lower binding constant for the floc with EDDS compared to that with EDTA.

Cadmium adsorption in the presence of PDTA, HDTA, CDTA and NTA

The results obtained in the previous sections are also mirrored by those obtained using a range of other chelates. Fig. 8 shows the variation of adsorbed Cd^{2+} with increasing chelate concentration for PDTA, HDTA, CDTA and NTA. Extending the alkyl-chain from C_2 to C_3, PDTA, resulted in similar results to EDTA. Maximum adsorption was achieved at equimolar proportions and, as with EDTA, the adsorbed Cd^{2+} is found to decrease at high chelate concentrations. Using HDTA, the adsorption limit for Cd^{2+} was only reached at a chelate concentration of 0.33 mM. In this case, the maximum Cd^{2+} removal was observed when the chelate concentration was approximately ten-fold greater than that of the Cd^{2+}. A similar result was observed for CDTA. In the presence of PDTA, HDTA and CDTA, only 80–86% of the Cd^{2+} could be adsorbed compared with >95% for EDTA and EDDS. Reducing the denticity of the chelate only changes the values of maximum adsorption but not the general shape of the curve. Using NTA, a maximum adsorption of Cd^{2+} of 67% is found when [NTA]/[Cd^{2+}] is approximately 1.5. In all cases the

Table 1 Constants used for eqns. (1)–(11) used in generating the curves in Figs. 3–7 (temperature 22 °C, experimental ionic strength 0.037 M and pH = 7; $x = 1$,[a] $y = 0$,[a] number of surface sites per Al atom = 0.08[a])

Chelate	$10^4\alpha$	$\log K_1$[b]	$\log K_2$[b]	$\log K_3$[a]	$\log K_4$[a]	$\log K_5$[a]
EDTA	8.05	13.51	13.29	−4.28	3.91	8.27
EDDS	2.39	11.62	7.60	−4.28	4.28	<2.4

Chelate	$\log K_6$[b]	$\log K_7$[b]	$\log K_8$[b]	$\log K_9$[b]	$\log K_{10}$[b]	$\log K_{11}$[b]
EDTA	−10.89	−12.20	−6.07	−17.25	−10.55	−5.30
EDDS	−10.89	−12.20	—	−17.25	−10.55	−5.30

[a] Constants fitted to observed results. [b] Constants taken from the references as described in the text.

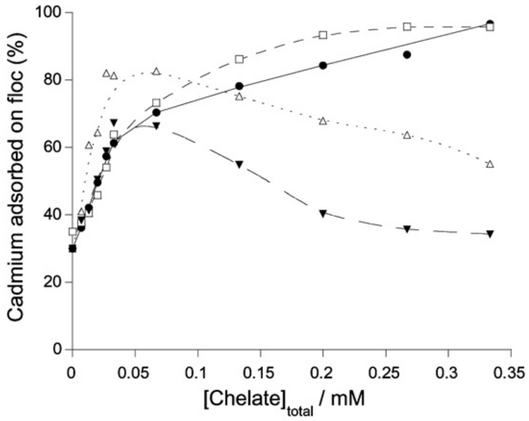

Fig. 8 Variation of %Cd contained in the floc with increasing HDTA (□), PDTA (△), CDTA (●) and NTA (▼) concentration formed from a solution adjusted to pH 7.0 containing 333 ppm Al and 3.33 ppm Cd (12.3 mM Al^{3+} and 29.7 μM Cd^{2+}) under co-precipitated conditions. The lines are schematic only and have been included to show the trend.

model can be fitted to the experimental data without major discrepancies.

Cadmium adsorption in the presence of PhDTA

Fig. 9 shows the variation in adsorbed Cd^{2+} with increasing PhDTA concentration at pH 7. As expected from the other chelates described above, a rapid rise in the adsorbed Cd^{2+} is observed as the chelate concentration is increased. However, compared with EDTA, the limiting metal adsorption is reached at a much reduced concentration of chelate. Only 0.0033 mM PhDTA is required to cause >95% Cd^{2+} adsorption. This corresponds to a ten-fold molar excess of *metal* over the chelate.

It is not possible to model this variation using the equilibria (1)–(11) in which it is assumed that the floc structure is unaffected by the presence of the chelate. The adsorption profile on co-precipitating with PhDTA qualitatively behaves like that of EDTA although only one tenth of the concentration of PhDTA is required to produce an equivalent shift of the pH edge. Fig. 10 shows the variation of adsorbed Cd^{2+} with pH when co-precipitated in the presence of PhDTA. As observed with EDTA, an increase in adsorption of Cd^{2+} increases with pH indicating cationic-like adsorption.

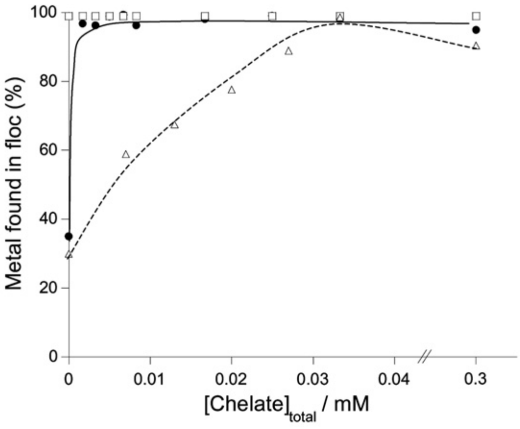

Fig. 9 Variation of %Al (□) and %Cd (●, solid line) contained in the floc with increasing PhDTA concentration formed from a solution adjusted to pH 7.0 containing 333 ppm Al and 3.33 ppm Cd (12.3 mM Al^{3+} and 29.7 μM Cd^{2+}) under co-precipitated conditions. The variation of %Cd (△, dashed line) with EDTA concentration is shown for comparison. The lines are schematic only and have been included to show the trend.

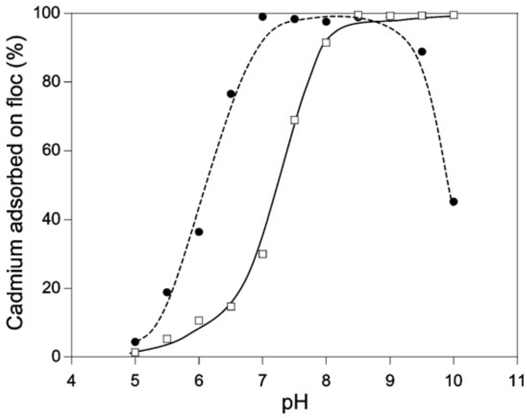

Fig. 10 Variation of %Cd adsorbed with increasing pH from a co-precipitated solution containing 333 ppm Al, 3.33 ppm Cd (12.3 mM Al^{3+} and 29.7 μM Cd^{2+}) and 3.3 μM PhDTA (●, dashed line) and distilled water (□, solid line). The lines are schematic only and have been included to show the trend.

Floc and adsorbate structure

It might be argued that the method of preparation should have little effect on the adsorption characteristics since all systems will reach a common equilibrium eventually but aluminium hydroxide polymorph equilibria are notoriously difficult to achieve.[34] On the other hand, in the co-precipitated system studied here, the results in Fig. 2 suggest that equilibrium is rapidly established. This is in good agreement with the extensive study performed by Dario and Ledin,[7] where the systems were equilibrated for various times up to 168 h and showed no time variation. The final structures formed here are kinetically stable even if they have not reached true thermodynamic equilibrium. It is noticeable that where adsorption varied strongly with time, the adsorbent had been dried prior to use. The equilibration times required become understandable since solid-state diffusion within the core of the particles then becomes the rate-limiting step.

It is worth noting that in every case except that of PhDTA, there is a steady progression, shown in Figs. 5, 7 and 8, from the normal adsorption to the maximum adsorption in the presence of chelate. In the case of PhDTA there is a sudden discontinuous increase, Fig. 9. Although it is possible to argue that a steady progression might occur at sufficiently low concentrations of PhDTA, the observed change is more like the transformation due to the nucleation and rapid growth of a different structural form of the hydrous aluminium floc than found in the other systems studied.

There is some evidence that this may indeed be the case. In the presence of PhDTA, the co-precipitated floc retains much more water on centrifugation than in the absence of a chelate or in the presence of smaller chelates such as EDTA or EDDS. On co-precipitation, the floc formed using PhDTA has a volume 15% larger than in all other cases, suggesting a change in the surface properties of the floc particles. This change in structure may simply be a strengthening of the hydroxide lattice, so as to enhance the water retention but any change in structure will also change the surface acidity slightly and alter the number of deprotonated adsorption sites. Structural changes due to the presence of chelates have been described previously. Szekeres *et al.* showed that adsorption of salicylate on alumina caused a disordering of the surface.[6,35,36] In that study, the strong chelating ability of the salicylate disrupts the surface order and changed the structure of the aluminium hydroxide formed.

The effect of PhDTA in reducing the pK_a of the surface will shift the pH edge observed for cadmium. Although a ternary surface complex is also likely to be formed at higher chelate concentrations, the additional enhancement will not be easily detected since the metal adsorption is already so high. Analogous changes in the adsorption constants with structural variations have been shown by Nowack *et al.*[14] By changing from hydrous ferric oxide to goethite, the pH edge for the adsorption of Ni–EDTA complex is shown to shift from 6.5 to 8.1. A slightly smaller shift in the pH edge from 7.5 to 8.4 is also observed changing from γ-Al_2O_3 to δ-Al_2O_3.

The results presented in this paper are in good agreement with a number of other studies where co-precipitation was used to form the floc. Dario and Ledin[7] observed cationic like adsorption for Cd^{2+} on ferric hydroxides in the absence and presence of fulvic acid. Bryce *et al.*[37] also showed that the component addition sequence for nickel adsorption of hydrous ferric oxide in the presence of EDTA altered the type of binding observed. For example, the addition of nickel to pre-formed hydrous ferric oxide followed by EDTA led to a cationic adsorption curve, whereas when nickel and EDTA were pre-equilibrated before mixing with hydrous ferric oxide, classical ligand-like binding was also observed. Cationic Cd^{2+} adsorption has also been observed in the presence of polyacrylic acid on γ-Al_2O_3[38] and on α-alumina based systems in the presence of the citrate anion.[39] In all cases the systems were equilibrated for extended periods of time.

Our general model for this cationic-like binding relies on the presence of an Al–O–M–L species on the floc. This was also proposed by Vohra and Davis[40] to explain a similar observation following the adsorption of Pb^{2+} on TiO_2 in the presence of nitrilotriacetic acid. In that study, cationic binding was also observed in the presence of the chelate, which could only be fitted using a Ti-O-Pb-NTA^{2-} surface complex.

It may be argued that the co-precipitation results presented in this paper depend on the preservation of an early form of adsorption possible only during the formation of the parent microfloc preceding aggregation but there can be no doubt that the product is robust, reproducible and stable. A detailed study[24] into the modes of aluminium hydroxide precipitation has revealed that the initially formed water-rich precipitate can be stabilised by anionic adsorbates. The same work has described the metastable phases by systems of balanced equilibria paralleling the approach used in this paper. As shown, the percentage of cadmium adsorbed follows a simple equilibrium scheme in all cases save that of PhDTA.

By adding a chelate it is possible to improve the efficiency of the removal of heavy metals by flocculation. However, it is only in the case of EDDS that this process may be viable for wastewater treatment. EDDS is not only biodegradable[32] but also can be used in excess without stripping the metal from the floc. By adding such a promoter, the concentration of heavy metals which can be removed increases without the need to increase the aluminium concentration.

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