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The application of montmorillonite clays impregnated with organic extractants for the removal of metals from aqueous solution
Part I. The preparation of clays impregnated with di-(2-ethylhexyl) phosphoric acid and their use for the removal of copper(II)

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Abstract

The adsorption of di-(2-ethylhexyl)phosphoric acid (DEHPA) into montmorillonite clays containing various interstitial (interlayer) inorganic and organic cations is described. The adsorption isotherms follow a step-like pattern with loadings, depending on the cation, approaching a maximum of 3 mol kg^{-1}.

The clay impregnated with DEHPA has been used successfully to remove copper(II) ions from aqueous solutions. The extraction isotherms also show a step-like pattern with the formation of both 2:1 and 1:1 extractant:copper complexes giving maximum loadings of about 0.5 mol kg^{-1} for a clay containing approximately 0.5 mol kg^{-1} DEHPA. The rate of extraction is reasonably fast with 15 min to reach equilibrium.

Losses of DEHPA from the impregnated clay under the conditions of extractant are also dependent on the nature of the interstitial cation and losses of $<$10 ppm can be readily obtained. Such losses indicate the potential for use in hydrometallurgical circuits and control of aqueous effluents from industry or land-fill sites. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Montmorillonite clays; Di-(2-ethylhexyl)phosphoric acid; Copper(II)

1. Introduction

Liquid–liquid extraction and ion exchange are well-established technologies for the recovery of metals from dilute aqueous product streams and effluents. However, both these techniques possess some disadvantages in use, thus, in liquid–liquid extraction the use of organic extraction reagents can cause problems with entrainment and solubility losses to the aqueous phase which can be transmitted into the environment. This is not a problem when using the solid ion exchange resins, but here the problems are associated with poor selectivity for particular metals and relatively slow kinetics of uptake. These problems can be overcome to a certain extent by impregnating these solid polymers with commercial liquid organic extractants. These resin impregnates have been extensively studied, but leakage of the extractant from the polymer has limited their commercial application. Alternative processes which have been devised to overcome such difficulties include the use of inorganic adsorbents, for example: hydroxides and oxides [1,2], zeolites [3], and clay minerals [4–6] for the extraction of lead, nickel, cadmium, zinc and copper. Adsorbents with a greater selectivity have been developed by either grafting functional groups onto a silanised silica gel support or by impregnation of supports with commercial metal extraction reagents [7,8].

There are a number of papers concerned with the impregnation of organic resins [11–14] and silica gel [7,8] with organic extractants to increase the selectivity of extraction, little has been published on similar experiments with clay minerals. As noted above clay minerals have featured as adsorbents and have the advantages of being both abundant and inexpensive. They possess a 2:1 or 1:1 layer structure resulting from the condensation of alternating silica tetrahedral (SiO_4) layers and aluminium octahedral layers [$Al(OH)_3$]. Isomorphous substitution of magnesium or iron(II) ions in the octahedral gibbsite-like layer or aluminium ions in the silica layer result in an overall excess of negative charge on the clay which is usually compensated

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with sodium and calcium ions in the interlayer spaces. The ability of such clays to undergo cation exchange with these interlayer cations has been used to treat metal contaminated wastewaters [4–6] or for adsorbing organic pollutants [9,10]. Although they possess a relatively large cation exchange capacity (CEC) for metals (~1 meq. g^{-1}) the lack of selectivity limits their practical application.

Several years ago a fire clay (kaolinite) impregnated with extractants such as tertiary amines and α-hydroxyoximes was proposed for hydrometallurgical applications [15,16]. More recently a highly leached clay was impregnated with 2-mercaptobenzothiazole for analytical pre-concentration [17] of metals, and thiol groups have been grafted onto montmorillonite clay for the selective extraction of lead, cadmium, mercury and zinc [18]. In this paper, the results of some studies on the removal of copper from dilute acid waters using a clay mineral impregnated with the widely used commercial liquid extraction reagent di-(2-ethylhexyl)phosphoric acid (DEHPA) are presented. No other studies related to the impregnation–intercalation onto clays of commercial acidic extractants appears to be available.

2. Experimental

2.1. Materials

Sodium montmorillonite, grade MPS-1, (Volclay Minerals Ltd., UK) with 99.75% montmorillonite content and 99% passing 20 μm, with a CEC 1 meq. g^{-1}, was used without further treatment.

Di-2-ethylhexylphosphoric acid, DEHPA (Aebright and Wilson) was used as received. Quaternary ammonium salts used to prepare homoionic clays were: tetramethylammonium chloride, TMACl, 98% puriss; tetrapropylammonium bromide, TPABr, 98% puriss; hexadecyltrimethylammonium bromide, HDTABr, 98% puriss.

Solutions of metals were prepared from analytical grade reagents (Analar) and diluted to the required concentrations in distilled water.

2.2. Preparation of homoionic clays

The sodium montmorillonite as supplied contained a small amount of calcium so to ensure complete substitution the clay was treated with an aqueous solution containing a three-fold excess of metal ions. The clay (50.0 g) was suspended in distilled water (3.0 dm^3) containing 3 meq. of the substituting cation (Na^+, Ca^{2+}, Cu^{2+}, TMA^+, TPA^+ and $HDTA^+$) in the halide form per gram of clay. The suspension was stirred for 48 h, centrifuged and washed free of excess ions with distilled water, as indicated by a negative silver nitrate test. The resulting material was dried at 110°C for 48 h, ground to pass a 200 mesh sieve (63 μm) and stored in a desiccator over $CaCl_2$. The CEC of the homoionic clays was determined using copper(II) as the exchangeable cation.

2.3. Intercalation of the clays

Homoionic clays as prepared above were contacted with a solution of DEHPA dissolved in a binary solvent of 1:1 ethanol:distilled water for 1 h with stirring. Kinetic experiments indicated that equilibrium was attained in 10–15 min, thus, 1 h contact time was selected to ensure that equilibrium was reached. A liquid:solid ratio of 40:1 was used to ensure complete dispersion, and the amount of DEHPA added, varied from 0.05 to 1.40 g g^{-1} clay. The materials were placed in stoppered glass tubes and mixed on a rotating wheel at 30 rpm for 1 h, this mixing was followed by centrifugation and the supernatant solutions analysed. The amount of DEHPA present in the original solution and after adsorption was determined by titration with standard alkali, and the amount adsorbed was calculated from the difference between these concentrations. The resulting intercalated materials were oven-dried for 48 h at 80°C, ground to minus 63 μm and stored in desiccators.

The products were characterised by X-ray powder diffraction and by diffuse reflectance Fourier transform infrared spectrophotometry (DRIFT) [19].

2.4. Metal loading capacity of the intercalated clays

Adsorption isotherms were determined for copper(II) in aqueous sulphate solution, using the clays intercalated with DEHPA. About 0.2 g of the solids were contacted with 20 cm^3 of the copper solution, in glass stoppered tubes and mixed on a rotating wheel at 30 rpm at 22 ± 2°C. The initial metal concentration varied from 100 to 8000 ppm, with no control of the solution ionic strength. The pH of extraction was maintained between 4.3 and 3.9 pH units by addition of 0.1 mol dm^{-3} sodium hydroxide solution. Previous studies showed that equilibrium was attained within 15 min, thus, a contact time of 1 h was selected to ensure equilibrated systems. After equilibration, the clay was separated from the solution by centrifuging and the solution analysed, either by ICP–AES or complexometric titrations with EDTA (0.02 mol dm^{-3}) using pyrocathecol violet as indicator.

All the above experiments were repeated at least three times, and the reported values represent the mean values.

3. Results

3.1. Clay-extractant intercalates

The experiments showed that all the homoionic clays adsorb DEHPA. Values for maximum adsorption depend on the nature of the interlayer cation and range from 2.78 mol DEHPA/kg clay for sodium montmorillonite to 2.21 mol DEHPA/kg in the case of copper montmorillonite. For the

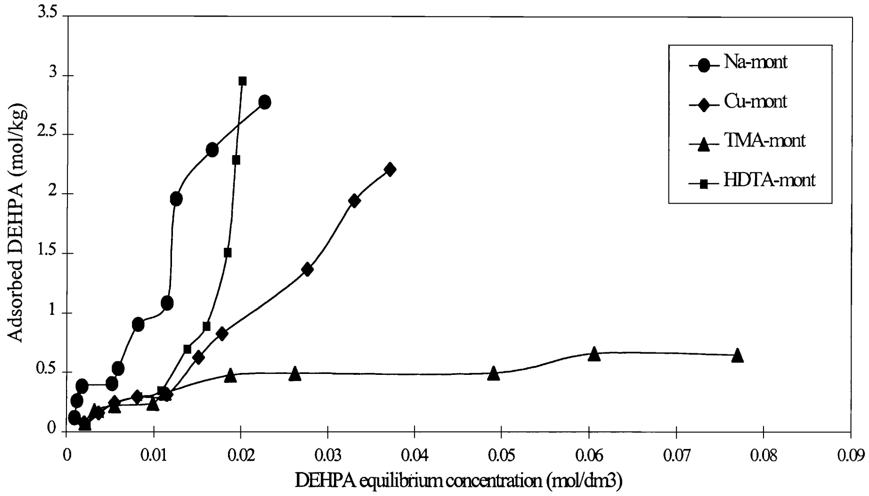

Fig. 1. DEHPA adsorption isotherms for modified monmorillonites.

alkylammonium clays, TMA-mont. and HDTA-mont. the values obtained are 0.64 and 2.96 mol DEHPA/kg clay, respectively. The resulting adsorption isotherms, Fig. 1, shows a stepped shape that reflects the different mechanisms governing the intercalation of the extractant onto the various montmorillonites. At higher DEHPA solution concentrations the clay assumes a shiny appearance suggesting that the DEHPA is now also being adsorbed on the external surfaces of the particles [19].

The X-ray powder diffraction studies of the intercalated clays confirm that the alkylphosphoric acid ester molecule is located in the interlayer spaces, producing an expansion of the *c*-axis of the clay structure, proportional to the dimension of the interlayer complex. Basal spacings between 1.66 and 4.65 nm were observed indicating the formation of mono- and bi-layers of extractant [19–21].

Infrared spectral analysis also confirmed the presence of the extractant on the clay with characteristic bands of DEHPA occurring in the spectrum of the clay [19]. Further details of the characterisation of the intercalates and adsorption mechanisms will be published elsewhere [22].

3.2. Copper extraction by homoionic clays

The inorganic and organic homoionic clays were exchanged with copper to assess their CEC and evaluate the effect of the interlayer cation on the availability of exchange sites on the clay. The results show that the CEC of the inorganic clays are close to the reported value of 1.0 meq. g^{-1} dried clay with the experimental values of 0.92 meq. g^{-1} (Na^+) and 0.88 meq g^{-1} (Ca^{2+}). In addition the amount of the desorbed interlayer cations was monitored to confirm the Cu^{2+} adsorption data. The resulting mass balances were within experimental error and indicated the process followed the law of mass action. The absorption isotherms, see Fig. 2 for Na-mont., have an 'L' shape indicating the occupation of all available sites for exchange [23]. The CEC value obtained for the Na-mont. is in very good agreement

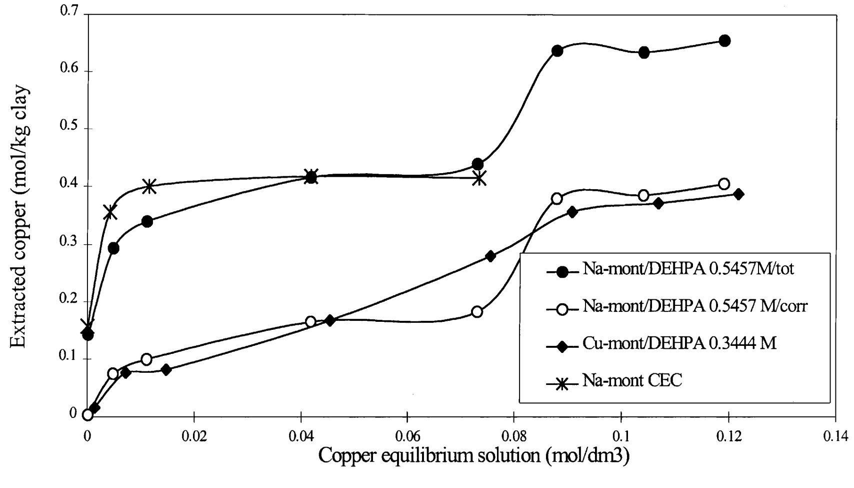

Fig. 2. Copper extraction isotherms for inorganic modified montmorillonites intercalated with DFHPA.

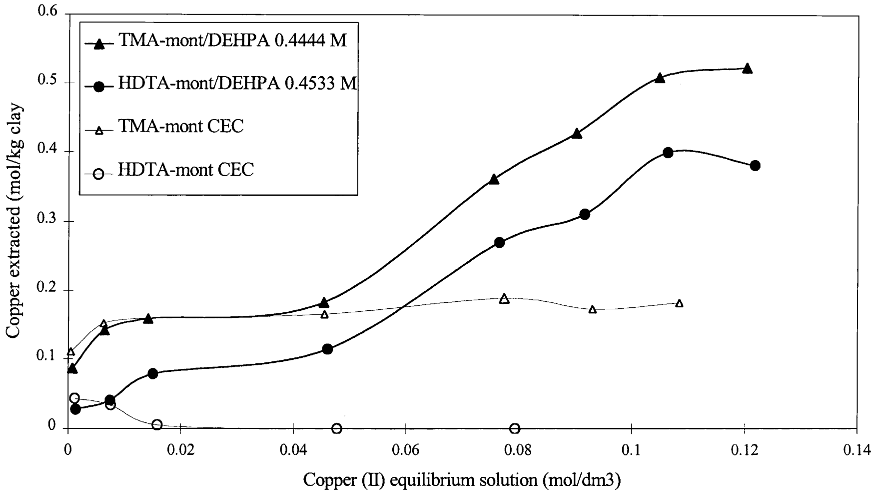

Fig. 3. Copper extraction isotherms for alkylammonium modified montmorillonites intercalated with DEHPA.

with a similar material where a value for Cu^{2+}/Na^{+} (ClO_4^{-}) of 0.92 ± 0.05 meq. g^{-1} was observed [24].

In the case of the alkylammonium clays, a different behaviour was observed. The exchange capacity of these clays is lower than the observed values for the inorganic cations. The difficulty of analysing the low concentrations of alkylammonium cations in the supernatent aqueous phase precluded the determination of the amount of exchanged ions. For the small TMA^{+} cation the observed value 0.42 meq. g^{-1} is approximately 46% of that for the inorganic cations. As the size of the organic cation increases the ability of copper to replace these cations decreases, thus, the CEC for the TPA^{+} clay is 0.34 meq. g^{-1} and in the case of the large $HDTA^{+}$ species only at low copper concentrations is there any exchange giving a very low value of the CEC, 0.09 meq. g^{-1} (Fig. 3). These results are in agreement with the general consensus that once located in the interlayer spaces such molecules are difficult to replace [25,26] and indicates the strong electrostatic and van der Waals interactions of these organic cations with the siloxane layers in montmorillonite and with each other. As the size of the organic molecule increases the van der Waals component increases [25] which is reflected by the inability of copper to replace the HDTA cation. Thus, using an organic interlayer cation as a substrate for the intercalation of organic extractant molecules results, as seen later, in better retention of the extractant during the recovery of metals from solution.

3.3. Copper extraction by inorgainc clays intercalated with DEHPA

For this series of experiments a standard clay was chosen obtained from a solution of DEHPA at an initial concentration of 0.0195 mol dm^3 in 1:1 ethanol:water intercalated for 1 h at room temperature. This intercalated clay contains a monolayer or near monolayer of the extractant (about 0.4–0.5 mol dm^3).

The copper extraction isotherms for the inorganic clays (Na^{+} and Cu^{2+}) are shown in Fig. 2, for clarity the data for Ca^{2+} have not been included. The pH of extraction was maintained at about pH 4.2–4.8, the highest possible under the solution conditions. This figure also includes the copper/sodium exchange for the homoionic clay for comparison (CEC about 0.4 mol kg^{-1}). The extraction of copper by the sodium and calcium clays intercalated with DEHPA was higher than that of the similar copper clay and was higher than the theoretical loading of copper by DEHPA as calculated on the basis of a $Cu(DEHPA)_2$ complex. It was also found that in the case of the Na^{+} and Ca^{2+} clays these cations were released into solution indicating that the DEHPA molecules did not replace all of the cations during intercalation. Fig. 2 shows the total copper loading and also as corrected for cation desorption in the case of Na^{+}, once such a correction is applied then copper extraction follows similar trends. The plots have an unusual shape, instead of the 'L' shape found for liquid–liquid extraction, solvent impregnated resins and CEC of the clays, the plots show two steps or plateaux of an 'S' shape isotherm. These are particularly well defined for the Na^{+}-mont./DEHPA clay with the Ca^{2+} and Cu^{2+} samples exhibiting less well-defined inflections.

At the first inflection of the isotherm, $[Cu]_{eq} < 0.076$ mol dm^{-3}, the total extraction of copper resembles that for the homoionic clays indicating the influence of the cation exchange sites and is accompanied by the desorption of Na^{+} and Ca^{2+} ions. This can be associated with 'non-selective extraction' and accounts for almost 58 and 52% of the total loading of the Na- and Ca-mont./DEHPA intercalates, respectively. The lower CEC value than that of the Na-mont. clay at $[Cu]_{eq} < 0.015$ mol dm^{-3} suggests that the free cation exchange sites have been modified and/or occupied by the DEHPA molecules. In the concentration range of this first inflection, the corrected copper loading values are: Na-mont., 0.183 mol dm^3 Ca-mont., 0.224 mol dm^{-3}, and

Cu-mont., 0.168–0.224 mol dm^3. In the latter case because all the cation exchangeable sites are already occupied by copper ions, the metal is extracted only by DEHPA and so a different shape of the isotherm is observed.

The region of the isotherm where maximum extraction occurs is found between $[Cu]_{eq}$ 0.087 and 0.122 mol dm^{-3}, with corrected maximum loading capacities of: Na-mont., 0.405 mol dm^{-3} Ca-mont., 0.408 mol dm^{-3}, and Cu-mont., 0.388 mol dm^{-3}. This order does not follow the $[DEHPA]_{clay}$. Because of variations in the sorption of DEHPA and slight variations in the experiments, the $[DEHPA]_{clay}$ values of the clay samples follow the order: Na-mont., 0.546 mol dm^{-3} Ca-mont., 0.467 mol dm^{-3} and Cu-mont., 0.340 mol dm^{-3}. When these variations in $[DEHPA]_{clay}$ are considered the following maximum values of ratio of Cu:DEHPA are observed: Na-mont., 1:1.4; Ca-mont., 1:1.2 and Cu-mont., 1:0.9. In liquid–liquid extraction such 1:1 charged complexes are consider non-extractable and only capable of short-lived existence at the aqueous–organic interface [27,28]. In addition there is usually a significant excess of extractant available to avoid formation of such species [29]. However, in a solid intercalated clay there is a limited amount of extractant distributed over a large surface area, therefore, the extractant interfacial area is maximised. Thus, the conditions for formation of charged 1:1 complexes might prevail at the high metal solution concentrations in the clay platelets. The presence of such charged species requires the neutrality of the clay surface to be maintained, thus, to compensate the excess positive charge another negative species should be adsorbed. In this system, the most likely species is the sulphate ion either in association with the metal complex or in the Stern electrical double-layer. Such adsorption has not been confirmed by analysis of the raffinate solutions and further experimentation is required. Such charged complexes have been reported in solvent impregnated resins ([30] and references therein) and supported liquid membranes ([31] and references therein), systems similar to the intercalated clays.

3.4. Copper extraction by alkylammonium clays intercalated with DEHPA

The alkylammonium homoionic monmorillonite clays were intercalated with DEHPA at similar levels to those for the inorganic clays discussed above, i.e. $[DEHPA]_{clay}$ TMA-mont.: 0.367 mol dm^{-3},TPA-mont.: 0.447 mol and HDTA-mont.: 0.432 mol dm^{-3} and the copper extraction isotherms were measured at pH values in the range 3.3–4.6.

The isotherms are shown in Fig. 3, excluding TPA-mont. for clarity, both for total copper extraction and also corrected for alkylammonium cation desorption. However, as explained above, because of analytical problems the correction has been performed by subtraction of the CEC for copper obtained for the organoclays. Finally, the extraction: metal ratios were estimated by subtracting the CEC for copper from isotherm copper loading data.

Like the inorganic DEHPA intercalates these organo-clays have unusual extraction isotherm shapes and maximum loading copper values greater than for the $Cu(DEHPA)_2$ complex. The 'S' shaped isotherm shows the two plateaux, but here the transition is less well defined. The first plateau with $[Cu]_{eq} < 0.046$ mol dm^{-3} is a region where some cation exchange with the organic cations is expected, and above this value of $[Cu]_{eq}$, the isotherm slowly increases to a second plateau. Values of the molar ratio copper:extractant for these two plateau regions are: TMA-mont.: 2.1, 1.1; TPA-mont.: 2.3, 1.0; HDTA-mont.: 2.1, 0.9, with the $[DEHPA]_{clay}$: TMA-mont.: 0.432 mol dm^{-3}; TPA-mont.: 0.447 mol dm^{-3}; HDTA-mont.: 0.367 mol dm^{-3}.

Further experiments are currently under way to clarify and establish the mechanism for metal extraction into the intercalated clays and confirm the presence of Cu:DEHPA 1:1 complexes.

3.5. Losses of extractant during metal extraction

The above results indicate that the extractant retains its metal extraction properties in the interlayer spaces and also exhibits higher extraction loadings than normal. However, before such materials can be accepted for hydrometallurgical or environmental clean-up operations, their active lifetime must be accessed. This has two implications, firstly, a cost on the process, but more importantly the environmental impact from release of the extractant into the environment via the aqueous raffinate. To measure the latter a series of measurements were taken of the concentration of DEHPA in the raffinates from the copper loading isotherms. The results of these experiments are shown in Fig. 4 as a plot of DEHPA concentration against ionic strength. The increase in $\log D$ with ionic strength is clearly related to the 'salting out effect' typical of organic compounds. In addition the observed variation of $\log D$ with the nature of the inorganic cation: $Na > Ca^{2+} > Cu^{2+}$ follows the order of extractant concentration in the clay, with the Na-mont./DEHPA exhibiting monolayer coverage of the surface. Evidence, to be published elsewhere [22], suggests that both ionic interactions with the clay and hydrophobic interactions between the extractant molecules are involved in the adsorption mechanism and that these interactions will be strongest with a complete monolayer of DEHPA over the surface. As the extractant coverage of the surface decreases then the hydrophobic interactions may also decrease giving rise to increased DEHPA losses from the interlayer and a decrease in $\log D$.

In the case of the alkylammonium clays similar behaviour is found with higher values of $\log D$ than for the inorganic clays. This is to be expected from the possibility of increased hydrophobic interactions between the alkylammonium cations and the DEHPA molecules. It should also be noted that the total number of carbon atoms influences the $\log D$ values in the order TMA (C4) $<$ TPA (C12) $\approx$ HDTA (C19).

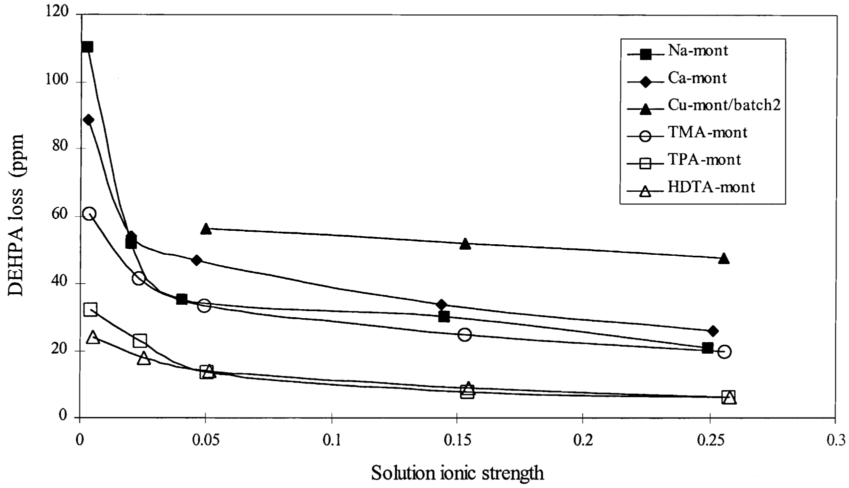

Fig. 4. DEHPA losses from intercalated clays as a function of solution ionic strength.

Table 1
DEHPA distribution values for losses from montmorillonite clays containing approximately 0.5 mol dm^{-3} DEHPA on acid extraction of copper at a clay solution ratio of 1:100

Clay	Na^+	Ca^{2+}	Cu^{2+}	TMA^+	TPA^+	$HDTA^+$
pH	4.73	3.99	4.30	4.23	3.83	4.29
Log D	5.52	5.63	4.93	5.43	6.02	5.98

The observed values of $\log D_{\mathrm{DEHPA}}$ in the raffinates following copper extraction are shown in Table 1 at the respective pH values of extraction:

These values are comparable with the losses of DEHPA from impregnated XAD-2 resin where $\log D$ values of 5.2 at pH 1.25 and 3.5 at pH 3.5 were recorded for an 0.05 mol dm^{-3} sodium nitrate solution [32].

As noted earlier the results also depend on ionic strength and a plot of DEHPA loss from the above clays in ppm against ionic strength is shown in Fig. 4. It should be noted here that the maximum value of the ionic strength shown is lower than would normally be expected in a leach liquor. Thus, the results show that the extractant losses from the clays are similar to or better than conventional liquid–liquid systems and so could be applied in hydrometallurgical flowsheets or in the treatment of metal containing effluents. However, such losses would not be acceptable for direct discharge into the environment and, thus, the inclusion of active carbon treatment downstream would be required as is common practice in water treatment for the removal of organic compounds.

4. Conclusions

These experiments have shown that layered clays impregnated with DEHPA provide a material with relatively fast kinetics and high loading capacity with the formation of 2:1 and 1:1 extractant:metal complexes.

Studies to be published elsewhere have shown that this process of impregnating clays with other types of acid extractant is widely applicable and that the selectivity of the extractants is maintained.

The high density of the impregnated material allows its potential application in hydrometallurgical flowsheets in clay-in-pulp extraction following suitable agglomeration thereby reducing the costs of traditional solid–liquid separation processes.

The impregnated clays can also be used as an 'active barrier' for the selective removal of toxic metal ions from land-fill leachates.

The extractant losses are small giving an appropriate active life-time for the material and minimising the environmental impact of the raffinates.

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