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Use of C-18 reverse-phase cartridges for estimation of metal complexation by a residue from olive oil industry

Abstract Formation of complexes between Cu and organic polymers present in olive mill wastewater (OMW) is shown to be a cause of metal solubilization by the residue, using C-18 reverse-phase cartridges (RPC) for separating the complexed metal. Nearly 100% of the metal released from a polluted river sediment by OMW solutions is retained by the cartridges. The proportion of Cu retained by the cartridges is somewhat lower (50–80%), if the OMW solution initially contains Cu. About 70–80% of Cu released by OMW from a soil column previously loaded with high doses of metal is also retained by the cartridges. Incomplete Cu retentions are not thought to be due to a lack of efficiency of RPC in immobilizing Cu complexes, but to the formation of an equilibrium between free and complexed forms of the metal.

Introduction

The presence of 'alpechín' (olive-oil mill wastewater, OMW) in waters in contact with metal-polluted sediments increase the solubility of such metals [1, 2]. The formation of soluble complexes between the metals and some humic-like organic polymers which are likely to be present in OMW is thought to be one of the causes for this enhanced metal solubility. Bejarano et al. [3] concluded by DPASV techniques that complexation of Pb(II) and Cu(II) by OMW does occur, and showed the labile behaviour of the complexes formed under certain experimental conditions. A detailed description of the main organic components of OMW has been given elsewhere [4].

A quantitative or semi-quantitative estimation of the contribution of such complexes to metal solubilization is difficult to achieve, especially due to their observed labile behaviour. The methods of Zunino et al. [5, 6], using a cation exchange resin, were found to be suitable for determining some characteristics of the complexes formed [7], when solutions of metal are titrated with OMW solutions or vice versa, but such methods are strongly model-dependent and, moreover, cannot be used for a direct distinction of complexed and uncomplexed metal released from a soil or sediment in contact with OMW.

Lee [8] and Mills and Quinn [9] used C-18 reverse-phase liquid chromatography for separation of metal-organic associates in natural waters, under the assumption that the retention of organic polymers by the C-18 cartridges must imply that any metal complexed by them should also be retained. In the present work, the use of C-18 reverse-phase cartridges is tested as a tool to separate complexed from free Cu when the metal is released by OMW solutions from a river sediment and from a soil which has received heavy doses of this metal.

Experimental

Materials

A sample of sediment was taken from the bank of the Agrio river (Seville province), near a mining area which has been known to cause occasionally high concentrations of heavy metals in the river waters at a short distance upstream from the sampling point. Further downstream the metals concentrations decreased sharply, showing that the sampling site is likely to be a point of accumulation of sparingly soluble metal forms. The sediment was air-dried and ground to pass a 2-mm sieve. Its cation exchange capacity (CEC) was $0.07 \ eq \ kg^{-1}$, organic matter (o. m.) content 1.0%, pH 7.4 and $CaCO_3$ content 13.3%. The total Cu content was $2880 \ mg \ kg^{-1}$. Sequential extraction by the method of Tessier et al. [10] showed that about 60% of the Cu content was bound to carbonate, and 30% was bound to iron and manganese oxides.

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A surface sample of a sandy soil (Typic Xeropsamment) was chosen. The soil was air-dried and gently ground to pass a 2-mm sieve. Its CEC was 0.039 eq kg^{-1}, o. m. content 0.14%, pH 8.5 and CaCO$_3$ content 8.6%. Thus, the retention of metal was likely to be due to the formation of sparingly soluble compounds to a greater extent than to cation exchange or complexation by its native o. m., considering the low values of CEC and o. m. content. The total Cu content was about 5.5 mg kg^{-1}, most of it bound to carbonates (about 60%) and in the exchangeable form (about 25%).

The OMW used was provided by the experimental plant of the Instituto de la Grasa y sus Derivados (CSIC, Seville). The original material was vacuum concentrated, freeze-dried and ground, and subsequently stored in a refrigerator. Immediately before each experiment, 5 g of the freeze-dried material were stirred with 100 mL of deionized water for 3 h on a magnetic stirrer and centrifuged at 30 000 g. A small fraction of solid remained undissolved and was discarded, and the solution was diluted to reach each desired concentration.

Methods

Metal release from the sediment. Duplicate subsamples of 0.5 g of sediment were placed in 1 L polypropylene containers and suspended in 500 mL of solution containing 1, 2 or 3 g L^{-1} of OMW. A parallel blank experiment was carried out suspending the sediment in water. The suspensions were shaken at 25 °C and aliquots were taken at various times between 3 h and 18 days of contact. The aliquots were centrifuged at 30 000 g for 20 min and the pH was measured in the supernatants. Two determinations of Cu concentration were carried out in separate portions of each supernatant: (a) after destroying organic matter by treatment with HNO$_3$; and (b) after passing 4 mL of the solution through 600-mg C-18 Sep-Pack reverse-phase cartridges (RPC), discarding the first mL. Metal concentrations were measured by AA spectrophotometry in both cases. The RPC were activated prior to their use by passing successively 5 mL of acetonitrile and 10 mL of water. In order to minimize the dilution of the samples when passing through the catridges, about 20 mL of air were passed through them to push the water out of the cartridges, without drying them out. In preliminary experiments, solutions containing between 1 and 30 mg L^{-1} of Cu were passed through the RPC in order to check that the metal was not retained, and negligible differences were found between the Cu concentrations before and after passing through the RPC.

In order to check whether the previous presence of Cu in the OMW solution had any influence on the release of the metal, a similar series of experiments was carried out in which the OMW solutions already contained 5 mg L^{-1} Cu.

Release of metal previously retained by the soil. Subsamples of 150 g of the soil were gently, uniformly packed into 4-cm diameter, PVC columns. The soil column was about 10 cm long. About 6 pore volumes of 0.01 mol L^{-1} KNO$_3$ were passed through the soil column in order to equilibrate the soil with the background solution. The sandy character of the soil caused a high permeability to water movement, therefore the flow rate was that determined by gravity. A peristaltic pump was adjusted to add solution at the same rate as it flowed through the soil, in order to maintain the soil at field capacity and avoid accumulation of solution above the soil column. After the KNO$_3$ solution, about 2 pore volumes of 0.01 mol L^{-1} KNO$_3$ solution containing 50 or 200 mg L^{-1} Cu as Cu(NO$_3$)$_2$ were passed through the column, followed by about 20 pore volumes of solution containing 10 g L^{-1} freeze-dried OMW. These high Cu concentrations were chosen because of the very high Cu retention power of the soil. Half-pore volume fractions were collected and analysed for Cu by AAS after the same two treatments (a) and (b) mentioned in the previous paragraph.

In preliminary experiments, it was found that when volumes greater than 5 mL of solutions containing 10 g L^{-1} of OMW were passed through the RPC, the resulting solution began to show some brownish colour, suggesting that the cartridges were close to saturation and OMW retention was not complete. Smaller volumes gave colourless solutions, therefore a volume of 4 mL was used for treatment (b) here as in the experiments with the sediment.

Results and discussion

Figure 1 shows the variation of solution Cu concentration versus the time of contact of the sediment with OMW solutions. The amount of Cu released from the sediment increases steadily up to about 5 days, after which a stabilization is observed. The amount of Cu in the plateau increases almost linearly as the OMW concentration increases: approximately 0.55, 1 and 1.2 mg L^{-1} Cu are released by 1, 2 and 3 g L^{-1} OMW solutions, respectively. The metal found in the solutions after passing through the RPC is much lower, and tends to zero after 2–3 days. The pH of all the solutions plotted in Fig. 1 were found to be between 7.2 and 7.6, so that any differences in Cu concentrations are not likely to be due to precipitation of sparingly soluble compounds, thus it is likely that most of the Cu released from the sediment is in complexed forms, if it is admitted that the RPC retain the complexed Cu but not the free metal. The solutions in contact with the sediment were also analysed for their Cu contents, prior to destruction of o. m., by DPASV [11], and the results were about 0.1 to 0.15 mg L^{-1} in all cases. The DPASV measurements are known to give an estimate of the free Cu in solution, although the interference of
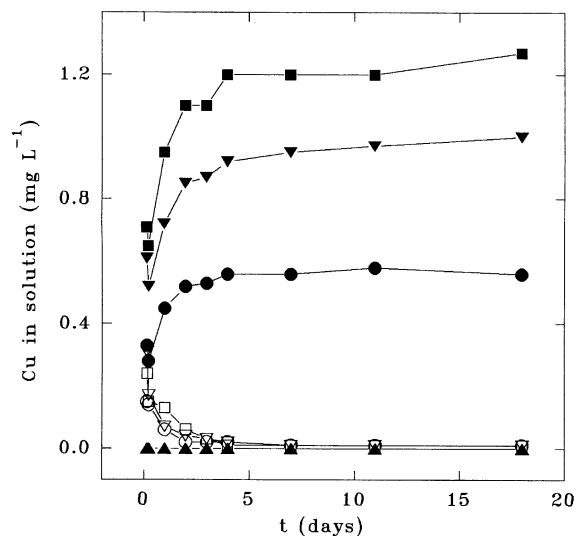

Fig. 1 Cu concentrations in OMW solutions in contact with the sediment (no Cu initially present). Full symbols, total solution Cu concentration; open symbols, Cu in solution after passing through RPC. Circles, 1 g L^{-1} OMW; inverted triangles, 2 g L^{-1} OMW; squares, 3 g L^{-1} OMW; upright triangles, blank experiments (water)
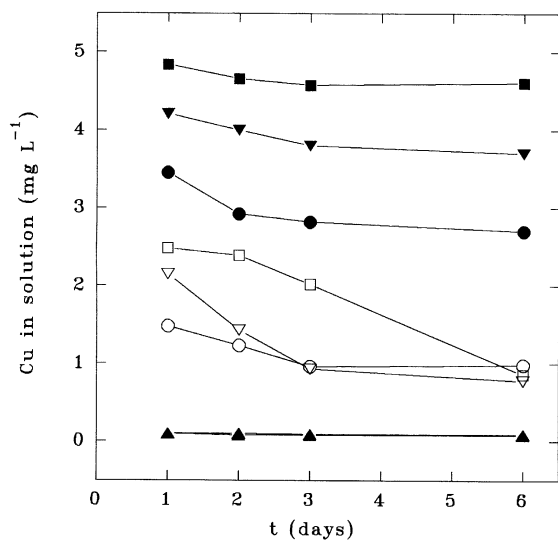
Fig. 2 Cu concentrations in OMW solutions in contact with the sediment (5 mg L^{-1} Cu initially present). Symbols as in Fig. 1

Fig. 3 Breakthrough curve of Cu added to a soil column (2 pore volumes of KNO$_3$ solution containing 200 mg L^{-1} Cu), and washed with OMW solution. Full line, total Cu in the solutions; dotted line, Cu in the solutions after passing them through RPC. Upper graph, proportion of solution Cu concentration retained by the RPC. Inserted: fraction of the Cu added which is released by the OMW solution

the o. m. of the OMW is likely to be significant and the values obtained must bear large errors. Therefore, the low results strongly suggest that most of the Cu present is complexed, in agreement with the RPC data.

Figure 2 shows the variation of Cu concentration with time when the OMW solutions originally contained 5 mg L^{-1} Cu. The resulting pH values of these experiments were always close to 7. It can be seen that the Cu concentrations are always below the added 5 mg L^{-1}, showing that the sediment retains part of the metal added with the OMW, although the amount remaining in solution depends upon the OMW concentration. Comparing full with open symbols in Fig. 2, it can be seen that the amounts of metal found in solution after passing though the RPC for the shorter times are about 50% of the total amounts, and this proportion decreases for longer reaction times down to about 20–40%. The variations after 6 days were negligible and the data for longer times are not shown. Therefore, the previous presence of 5 mg L^{-1} Cu in the OMW solution limits Cu release from the sediment, and even part of this Cu initially added to the system is taken up by the sediment, but a major proportion of Cu in solution (up to 80%) seems to be in complexed forms.

Figure 3 shows the breakthrough curve for a soil column which received a pulse of 2 pore volumes of Cu(NO$_3$)$_2$ solution and subsequent washing with OMW solution. The ordinates represent the Cu concentrations in the various fractions, expressed as fraction of the Cu concentration in the pulse of Cu solution initially added, C$_0$ = 200 mg L^{-1}. After 20 pore volumes of OMW, about 74% of the total Cu added was released. The pH values of the fractions collected were always within the range 6.6 ± 0.2. In a previous experi-
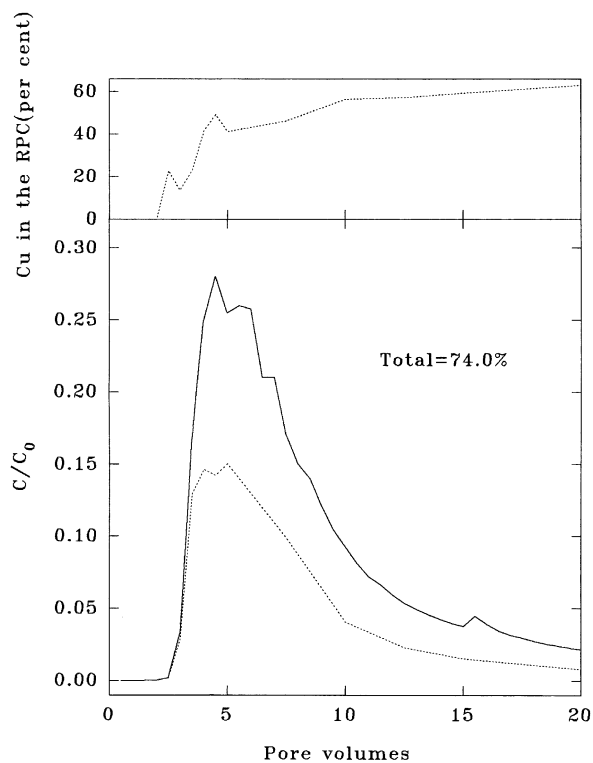
ment, it was found that when the washing was carried out with OMW-free KNO$_3$ solution the Cu concentration was never above C/C$_0$ = 0.002 and the total Cu released after 20 pore volumes was about 0.24% of the total added, showing that about all the metal was strongly held by the soil column and could not be washed by a simple electrolyte. The dotted line represents the data after passing the collected solutions through RPC. In the upper part of Fig. 3 the proportion of the Cu solution concentration in the leachate which is retained by the RPC is plotted as a function of the pore volumes. It can be seen that this proportion, presumably complexed Cu, increases up to about 60%, similar to, but slightly lower than the proportion complexed in Fig. 2. This lower proportion complexed could be due to the slightly more acidic pH, which will cause a lower dissociation of the active groups in the organic polymers and a consequently lower complexation capacity.

Figure 4 was obtained similarly to Fig. 3, except that the pulse of Cu solution added in the beginning of the experiment contained 50 mg L^{-1}. This experiment was carried out with the purpose of checking whether the amount of Cu could have any influence on the results.
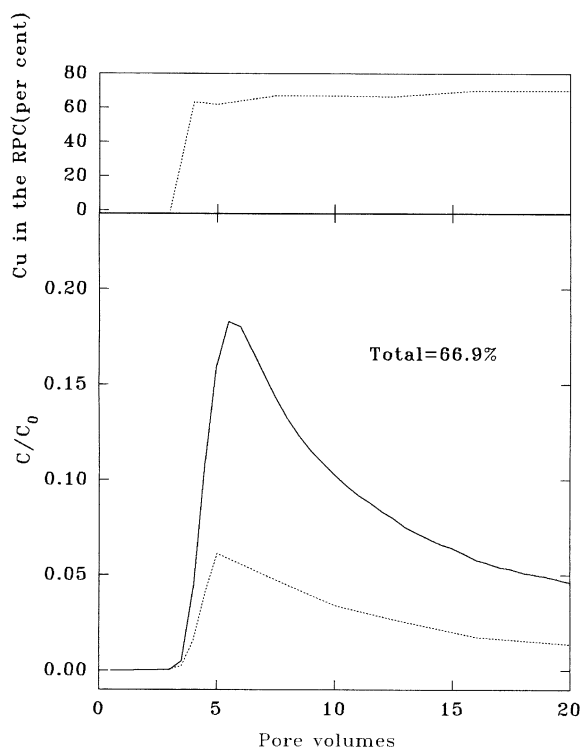
Fig. 4 Breakthrough curve of Cu added to a soil column (2 pore volumes of KNO$_3$ solution containing 50 mg L^{-1} Cu), and washed with OMW solution. Other details, as in Fig. 3

Although some minor differences are found when compared with Fig. 3 (e. g. a lower proportion of Cu recovered, 67% of the total added, and a slightly higher proportion of metal taken up by the RPC, $\geqslant 70\%$ of solution Cu concentration), the general features of Figs. 3 and 4 are similar. The breakthrough curve shows a rather more marked tailing than that in Fig. 3, which could be due [12] to a slightly greater difficulty for the OMW to release Cu. This reason can also explain the lower Cu recovery. The pH values of the leachates in this experiment, within the range 7–7.2, could cause a slightly higher complexation capacity of the OMW in this case as compared to that in Fig. 3.

General discussion

The results described in the preceding section show that the RPC can be useful for an estimation of the proportion of Cu complexed when sparingly soluble forms of the metal present in a sediment and a soil are solubilized by OMW solutions. It has been shown [2]

that the amounts of metals released by OMW are comparable to those fractions defined as exchangeable and bound to carbonates. In those cases where the proportion of Cu taken up by the RPC is not 100% of that present in solution (Figs. 2 to 4), two possibilities arise, (a) part of the metal is not complexed, or (b) part of the complexed metal is not retained in the RPC. The labile character of the complexes formed [3] could perhaps cause that part of the complexed metal behave as if it was not complexed, but the fact that in Fig. 1 all the metal present in solution is retained by the RPC suggests that this lability does not prevent the complexes from being retained in the experimental conditions used here. Moreover, total Cu concentrations in those cases where Cu retention by the RPC is not complete (Figs. 2–4) are always significantly higher than in those showing 100% retention (Fig. 1). Therefore, incomplete retention of the metal in solution by RPC is likely to be caused by incomplete complexation and not to lack of efficiency of RPC for retaining the complexed metal. In fact, it has been shown elsewhere [13] that the data of Fig. 2 fit a mononuclear-bidentated complexation model between the 'average' ligands present in OMW and the metal, assuming an equilibrium in which the amounts retained by the RPC correspond to the metal complexed and the metal remaining in the solution after passing through the RPC is free, uncomplexed metal.

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