

Effect of different extracting solutions on the electrodynamic remediation of CCA-treated wood waste Part I. Behaviour of Cu and Cr

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Abstract

Removal of Cu and Cr from chromated copper arsenate (CCA)-treated wood waste under batch electrodynamic conditions was studied. The effect of different types of extracting solutions, such as deionised water or aqueous solutions of NaCl, formic acid, oxalic acid, and EDTA, on the magnitude and direction of the fluxes of Cu- and Cr-containing species in the electrodynamic cell was investigated. Oxalic acid was found to have the best performance if simultaneous removal of the two elements is required (removal efficiencies of 80.5% for Cu and 87.4% for Cr, respectively). A mixture of oxalic acid and formic acid also led to similar removal efficiencies. In these experiments, the target elements were accumulated in both the anode and cathode compartments of the electrodynamic cell due to the formation of negatively charged complexes with the organic acids used besides the free cationic forms. The latter were not present if EDTA was the extracting solution resulting in directing the Cu and Cr fluxes to the anode compartment. Contrary, these fluxes were exclusively to the cathode compartment if deionised water or an aqueous solution of NaCl were used. These extracting solutions proved suitable for solubilising (re-mobilisation) of Cu but were less efficient for Cr removal (less than 20% removal). Overall, the results obtained show the important role of the proper selection of the type and composition of the extracting solution for the success of subsequent electrodynamic removal of Cu and Cr from CCA-treated wood waste. © 2003 Elsevier B.V. All rights reserved.

Keywords: CCA-treated timber waste; Electrodynamic remediation; Cu; Cr; Organic acids; NaCl; EDTA

1. Introduction

In the wood preservation industry, chromated copper arsenate (CCA) is still the most widely used preservative [1]. The corresponding annual release of CCA-treated wood waste, which is in the order of millions of tonnes, is considered rather large [2–4]. Various formulations of CCA-treated wood have been developed, incorporating different concentrations of chromium, copper, and arsenic but the most widely used of them is the so-called CCA Type C, containing 47.5% chromium as CrO₃, 18.5% copper as CuO, and 34.0% arsenic as As₂O₅ [4]. Accelerated

metal leaching may occur from CCA-treated wood and cause contamination of soils, located below or close to the storage areas, where the freshly treated wood is left for dripping-off the excess preservatives, as well as from the piles of impregnated wood caused by rain water, especially such of low pH [5–7]. The possible risk of subsequent contamination of groundwater and/or aquatic environment is also high [8–10]. Furthermore, exposure to CCA-treated wood waste poses a potential health hazard for the workers involved, because of the toxicity and cancerogenicity of Cr and As [11]. Therefore, the presence of large amounts of CCA-treated wood waste and drawbacks of the traditional land filling, as pointed out by the new European legislation, e.g., Directive 1999/31/EC [12], require urgent effective alternatives for remediation of this waste, and its possible reuse.

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So far, different approaches of treating CCA-treated wood waste have been suggested, such as incineration [13], low temperature pyrolysis [14], biological [3,15] or biochemical treatment [16], all showing different degrees of economic success and environmental relevance. In our previous investigations, an electro-dialytic treatment, performed under appropriate direct current conditions, proved to be a promising alternative for heavy metal remediation of polluted soils [17] and, more recently, for remediation of CCA-treated timber waste in the form of sawdust [18] or wood chips [19]. Basically, this method requires the availability of the contaminants in a soluble form in order to guarantee their removal, due to electromigration and/or electroosmosis, from the CCA-impregnated wood material. A pre-treatment of the polluted material with an extracting solution could improve the process efficiency, being the choice of the composition and concentration of the extracting solution(s) of utmost importance for the success of the subsequent electro-dialysis operation.

In our previous study, some dependencies of the electro-dialytic process behaviour, when deionised water or an aqueous solution of oxalic acid were used as the extracting solution, were elucidated and the direction and magnitude of the individual element fluxes to the anode or cathode cell compartments have been revealed in specially designed experiments, performed under dialytic (no external power supply) and electro-dialytic conditions (with external power supply) [19]. While, as expected, an electric potential difference applied between electrodes increased the ionic fluxes, the nature of the extracting solution was found to control the direction of the fluxes through the ion exchange membranes to the two compartments and the individual metal removal efficiencies.

Due to probable formation of negatively charged complexes between metal cations and oxalic acid, the anionic fluxes to the anode compartment dominated. However, since dissociated organic acid ions can serve also as an electric current-carrying medium it is not easy to evaluate the contribution of such complexes to the overall process behaviour. Therefore, in order to clarify the role of the extracting solution in the mechanism of the electro-dialytic removal process, comparison of different metal extracting solutions, including also no complex forming ones, is required.

Unfortunately, the literature dealing with this topic with respect to CCA-treated solid wood waste is limited. A laboratory study of a solely extraction process for pre-treatment of municipal solid waste incinerator fly ash to re-mobilise Cr, Cu, Pb and Zn gave promising results, especially in the case of chelating agents, which actions were pH-independent [20]. Several other studies dealt with the influence of some organic acids on heavy metals removal from CCA-polluted timber wastes [16,21,22]. However, not much is still known about the chemistry and speciation of the effects on the electro-dialytic remediation processes if organic acids, chelating agents or only electric current supporting solutions (e.g., NaCl) are applied as extracting solutions.

Therefore, the purpose of this work was to improve the understanding of the performance of coupled solubilisation/extraction and subsequent electro-dialytic removal of Cu and Cr from CCA-treated solid wood waste. The behaviour of As will be the subject of a forthcoming paper. The approach used was based on comparing the effects of different extracting solutions, containing: organic acids (single or in mixtures), EDTA as a chelating agent, NaCl as a “pure” current-carrying medium, and deionised water as a reference, on the subsequent preferential flow direction of Cu- and Cr-containing species, and the overall removal efficiencies for these two elements under electro-dialytic conditions.

2. Materials and methods

2.1. Polluted material

Laboratory experiments were carried out with CCA-treated wood chips, prepared from 20 years out-of-service *Pinus pinaster* Ait. Pole. The average dimensions of the chips were as follows: length 10–15 mm, width 2–10 mm, thickness ~1 mm, and the fine powder fraction contained was around 10%. The total target metal contents in the timber waste were: Cu—1.68 g kg⁻¹ (±0.07), Cr—1.49 g kg⁻¹ (±0.08), and As—1.95 g kg⁻¹ (±0.01), as determined according to Method 1 of the British Standard [23].

2.2. Laboratory cell

Batch laboratory remediation experiments were carried out in an electro-dialytic (ED) cell schematically shown in Fig. 1. The cell was developed at the Technical University of Denmark [24] and is described in detail elsewhere [17,24]. The ED cell consists of three compartments—two electrode compartments and a central compartment separated by two ion exchange membranes: a cation exchange membrane IC1-61CZL386 and an anion exchange membrane IA1-204SXZL386, both supplied from Ionics Inc., USA. For all experiments, the central compartment, where wood chips were placed, had a constant length of 30 mm and an internal diameter of 80 mm. Platinum-coated electrodes with a diameter of 3 mm and length of 50 mm from Bergsoë AC, Denmark, were used as working electrodes (cathode and anode, respectively). A power supply (Hewlett-Packard E3612A, USA) was used to adjust the desired initial direct current (DC) between the electrodes, as monitored by a Fluke 37 multimeter.

2.3. Experimental conditions

The CCA-treated wood chips were placed in the central compartment of the ED cell after their static incubation in the extracting solution under study for 24 h. Appearance of voids and gaps in the electro-dialytic cell was avoided by careful packing of the chips. The packing procedure was

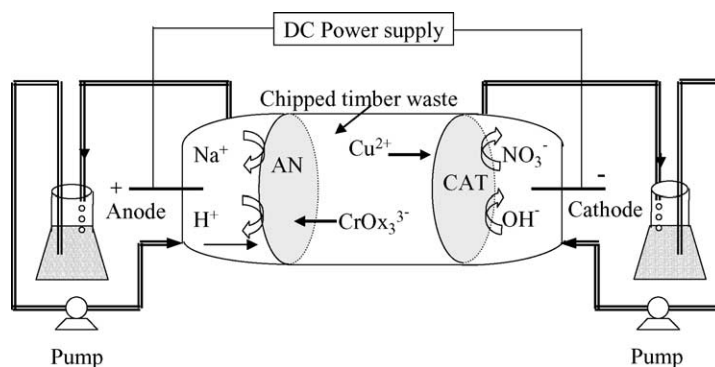


Fig. 1. Schematic representation of the electro-dialytic (ED) cell used (AN—anion exchange membrane, CAT—cation exchange membrane).

facilitated by the fact that the chips had been already saturated in the extracting solutions investigated. A liquid/solid phase ratio of 8.8 (w/w) was kept constant for all experiments as in our previous studies [19], incubating 40 g of CCA-treated wood chips in the extracting solution under study. Six extracting agents were studied: (a) Deionised water (DW); (b) 2.5% oxalic acid (OA); (c) 5.0% formic acid (FA); (d) a mixture of 2.5% oxalic acid and 5.0% formic acid solutions in a ratio 1:1 (w/w) (OA + FA); (e) 2.5% EDTA disodium salt—“IDRANAL III”, Merck (EDTA); and (f) 1.25% sodium chloride (NaCl). The concentration of NaCl was chosen to “mimic” the conductivity offered by the oxalic acid solution alone, in order to distinguish a possible oxalate complexes contribution to the process performance from that of the electric current alone. Nine experiments, six under electro-dialytic and three under dialytic (no external power supply) conditions were performed as summarised in Table 1. The experiments are designated by an abbreviation referring to the type of the extracting solution used (i.e., DW, OA, etc.). The three dialytic experiments are named DW (d), OA (d) and OA + FA (d) in order to distinguish them from the corresponding electro-dialytic ones.

Through each electrode compartment, 11 of 10^{-2} M NaNO_3 solution was re-circulated by a multi-channel peristaltic pump (Watson Marlow 503 U/R, USA). Constant flow rates of 0.61h^{-1} to both electrode compartments were maintained. The pH value of the catholyte solution, increasing due to accumulation of OH^- groups at the cathode, was

adjusted to about 3 by periodic addition (usually daily) of a few drops of a concentrated HNO_3 solution. The time duration of all experiments was set to 14 days.

Samples from the two electrode compartment solutions (catholyte and anolyte) were collected periodically and stored in refrigerated PVC vials. At the end of each experiment, the metals retained by the two ion-exchange membranes used were extracted by immersing each membrane in 100 ml of 1 M HCl solution for 48 h. Metals deposited on the electrodes were similarly extracted in solutions, obtained after immersing each electrode in 25 ml of 1 M HCl solution and applying a potential reversal against a clean electrode. Small amounts of wood chips after each experiment were also collected and treated for analysis.

2.4. Analytical methods

The total contents of Cu and Cr in the electrode compartment solutions, and in the solutions, obtained after immersing the ion exchange membranes and electrodes were determined by atomic absorption spectrometry (Perkin-Elmer 300-AAS). The final “total” amount of each element in the wood chips before and after the experiments was similarly analysed by AAS, however, after obtaining the respective element in a soluble form, according Method 1 of the British Standard [23]. All values reported in the paper are obtained on the basis of at least three replicated measurements (often up to five) and have relative standard deviations of less than 5%.

Table 1
Extracting media and experimental conditions

Experiment	Extracting solution	Concentration (%)	Conductivity (mS cm^{-1})	Initial pH	Initial current (mA)
DW	Deionised water	—	0.001	5.6	11.6
DW (d)	Deionised water	—	0.001	5.6	0.0
NaCl	NaCl	1.25	23.0	5.7	40.0
OA	Oxalic acid	2.50	25.5	1.2	40.0
OA (d)	Oxalic acid	2.50	25.5	1.2	0.0
FA	Formic acid	5.00	6.5	1.9	40.0
OA + FA	Mixture OA/FA (1:1)	2.50/5.00	23.5	1.4	40.0
OA + FA (d)	Mixture OA/FA (1:1)	2.50/5.00	23.5	1.4	0.0
EDTA	EDTA	2.50	7.7	4.4	40.0

(d): dialytic conditions (no external power supply).

3. Results and discussion

3.1. Effect of extracting solution on the dynamics of voltage drop in the ED cell

An applied electric potential difference between electrodes, located in or out of a polluted material, promotes the movement of ions and charged particles, contained in this material, by electromigration, electroosmosis, electrophoresis and electrolysis [25]. The initial values of this cell parameter in the electro-dialytic experiments (without considering Experiment DW, in which deionised water was used) were relatively low and all lied around 20 V regardless of the extracting solution applied. However, the following time evolution of the voltage drop was found to be strongly dependent of the type of solution used that is an indication of its significant impact on the process performance. After an initial weak decrease of the voltage drop through the ED cell (Fig. 2), a sharp increase was observed with a maximum plateau value, and a rate of approaching it, specific for each experiment. Probably, at the beginning of electro-dialysis operation, there were enough available charge particles (individual ions and/or their complexes with dissociated ions of organic acids, salts, and chelating compounds) [18,19] present in pre-treated material placed in the ED cell central compartment. Only, the electro-dialytic system in Experiment DW, in which the wood chips pre-incubation had been performed with deionised water, kept its initial high voltage value, that changed only slightly with time (from 82.6 to 87.5 V) (Fig. 2b). Obviously, besides its very low conductivity, deionised water has a rather limited potential to re-mobilise (solubilise) the elements in the CCA-treated solid wood waste.

When aqueous solutions of organic acids (single and/or in mixture) were used as extracting solutions, different time intervals were needed to reach the maximum voltage drop values, and the longest 1–6 days was detected for Experiment OA + FA (Fig. 2a).

The voltage drop kinetic curves for the experiments, performed with “pure” electrolyte supporting solution (NaCl)

or EDTA, acting also as an extracting (complex-forming) agent, showed faster maxima reached during the first day of operation. In the case of NaCl, the maximum voltage drop reached a value of 140 V, which is the limiting voltage possible with the external power supply used. On the other hand, the voltage drop stabilised around 50 V in the case of EDTA as the pre-incubating solution (Fig. 2b).

All these results show the important role of the extracting solution for the contaminants mobilisation and as an electric current carrier in the system that, as already mentioned, contains two ion exchange membranes, for which some specific interactions and probable preferred retention of organic ions of higher size can be expected. This may contribute to the higher voltage drop observed for oxalic acid, which dissociates to ions of a higher size than those formed in the case of formic acid.

Since the electric current passing in the ED cell is proportional to the electric potential difference (voltage drop) applied between the electrodes (according to Ohm's law), the initially set current value of 40 mA was kept during the whole operation time only in the processes with formic acid and EDTA, as extracting solutions, in which the voltage drop was relatively low (Fig. 3a and b). In all other cases, due to higher ohmic cell resistance, the power supply could maintain a direct current of 40 mA only in the beginning of these experiments, and it was not able to provide a sufficiently high voltage in the experiment with deionised water (the maximum possible current value was 11.6 mA), obviously, because of the very low amount of charge compounds able to carry electric current in the ED cell under such conditions. On the other hand, organic acids and EDTA, used for solubilisation/extraction of the target elements from the CCA-treated wood chips can increase the total amount of charge compounds in the central cell compartment of the ED cell in the form of individual ions as well as their complexes with the above-mentioned agents. These charge compounds can support for longer time periods an electric current passage in the ED cell.

If organic acids (or their mixtures) are used as extracting solutions, a low pH promoted liberation of metal cations can

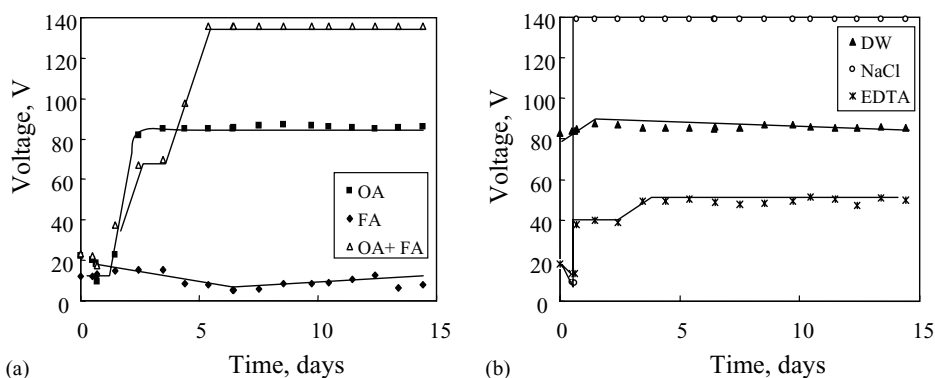


Fig. 2. Time course profiles of voltage drop through the ED cell in experiments with different extracting solutions: (a) OA, FA and OA + FA; (b) DW, NaCl and EDTA.

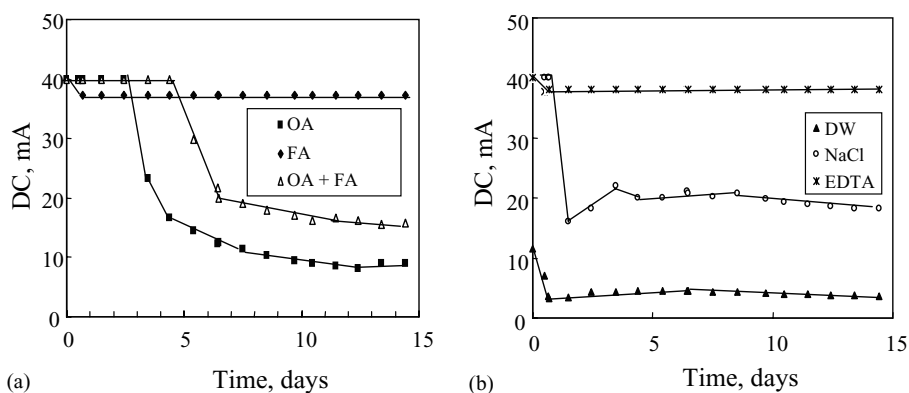


Fig. 3. Time course profiles of direct current passing in the ED cell in experiments with different extracting solutions: (a) OA, FA and OA + FA; (b) DW, NaCl and EDTA.

be expected besides formation of acid–metal complexes, depending on the type of acid applied. Previously, the major importance of providing a low pH environment for a successful electroremediation process has been suggested [26]. The latter was associated with a movement of an acidic front (resulting from the generation of protons due to water electrolysis at the anode) through a heavy metal polluted material. Therefore, it is interesting to assess the relative contributions of these two mechanisms: single acidic solubilisation (due to the low pH front) and complex formation (if suitable agents are present) for the overall electrochemical process performance. The impact of these mechanisms could be evaluated if an electrolyte solution of neutral pH and no complex formation potential (e.g., NaCl) is used as an extracting solution. In the latter case, the fastest current drop was observed (Fig. 3b). A similar tendency was reported for an electrokinetic soil washing experiment [27], based on the anode-generated acidic front, solubilising and removing metals when passing through the soil. Some authors [26,28] suggest that the meeting of this acidic front with the opposite basic front, generated at the cathode, can cause the drop in current. At that point of water formation (H^+ reacts with OH^-), precipitation of insoluble metal hydroxides or complexes is possible, thus, leading to a higher overall resistance of the cell. In result, the electromigration/electroosmosis phenomena and, therefore, the metals removal efficiency from the polluted material may become slow [29]. Thus, the higher potential of using extracting agents as extracting solutions in our study, compared to processes relying exclusively on the acidic front passage for “cleaning” the polluted material, is demonstrated.

3.2. Effect of the extracting solution on the dynamics of Cu and Cr concentration in the re-circulating solutions under dialytic conditions (no external power supply)

If no electric potential difference is applied between the electrodes (no external power supply), the movement of charged compounds from the wet wood chips, placed in the central cell compartment, to the re-circulating solutions is

controlled solely by the chemical potential differences for the species in the cell. In any case, the two ion exchange membranes are still serving as selective barriers for the transport of anionic or cationic species to the respective re-circulating solutions. For simplicity and easier comparison with the data obtained in the electrochemical experiments, however, we will still designate the solution contacting the anion-exchange membrane as “anolyte” and that contacting the cation exchange membrane as “catholyte”. The time dependent concentration curves for Cu and Cr accumulation in the “anolyte” and “catholyte” solutions under dialytic conditions are presented in Fig. 4a–d. These data show prevailing transport of Cu and Cr-containing compounds towards the “anolyte” solution in the experiments, using organic acids as extracting solutions. In Experiment OA (d), performed with an oxalic acid solution, the maximum concentrations of both target elements in the “anolyte” were around 4 mg l^{-1} , and the Cu concentration in the “anolyte” in Experiment OA + FA (d), performed with a mixture of formic and oxalic acid, was around 2 mg l^{-1} . In these two cases, the most probable reason for such transport behaviour is the availability of negatively charged species in the pre-incubated wood chips. Hexavalent chromium anionic compounds, such as $HCrO_4^-$; $Cr_2O_7^{2-}$; CrO_4^{2-} are well soluble and mobile and compounds like $CuOx_2^{2-}$ are rather stable [15]. Presence of other oxalates, such as $CrOx_3^{3-}$, is also possible.

In general, Cr-containing species were more slowly transferred, than Cu-containing ones, to the two dialytic cell re-circulating solutions and higher amounts of Cr remained in the treated chips after these experiments. Concerning the transport of Cu, a tendency of its movement through the cation exchange membrane towards the “catholyte solution” was detected even if deionised water is the extracting solution, Experiment DW (d), in spite of its rather low concentration in the re-circulation solution. This indicates that free Cu^+ and Cu^{2+} cations might have been liberated from the wood chips due to water solubilisation. Indeed, for this element, only pre-incubation with water was found to be sufficient for its re-mobilisation [19].

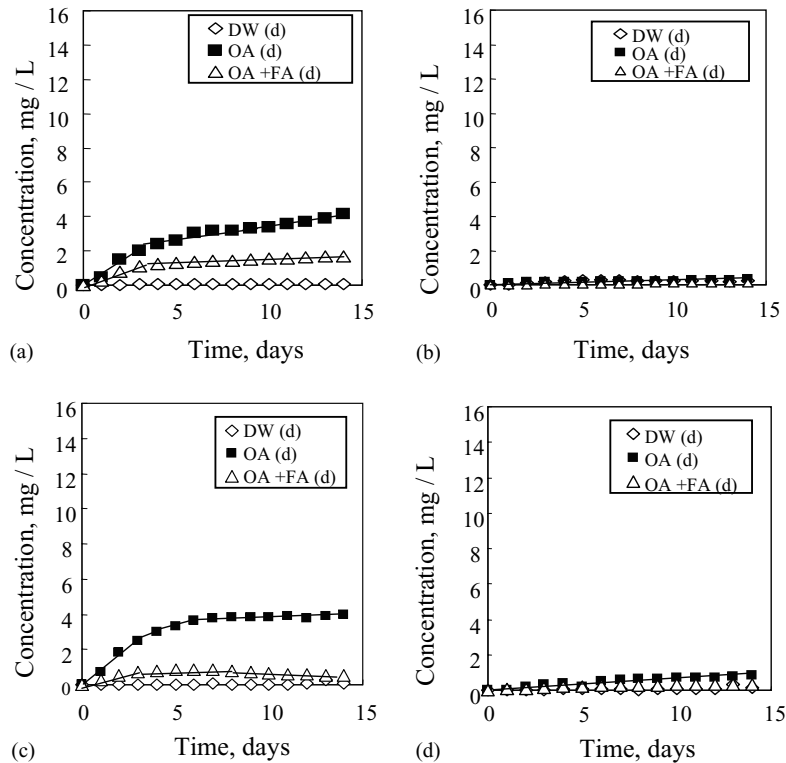


Fig. 4. Dynamics of Cu and Cr accumulation in the re-circulating solutions in experiments with different extracting solutions under dialytic conditions: (a) Cu in the anolyte; (b) Cu in the catholyte; (c) Cr in the anolyte; (d) Cr in the catholyte.

However, the relatively low target element concentrations in the re-circulation solutions demonstrated their slower mobility under dialytic conditions. Therefore, in order to increase the transport rates of Cu and Cr (as single cations or complex species) and, hence, their removal efficiencies, electro-dialytic conditions were required.

3.3. Effect of extracting solution on the dynamics of Cu and Cr concentration in the re-circulating solutions under electro-dialytic conditions (with external power supply)

The use of acidic extracting and complexing agents, showing strong affinity towards metal ions, is a common

technique for separation and recovery of metals from various sources. For remediation of Cu and Cr from CCA-treated wood waste, the suitability of using some organic acid solutions for pre-incubation, have also been shown [19]. Since the current in electro-dialysis is presented by the ion fluxes in the system under the influence of an externally applied electric potential difference [30], strong dependence between the current and Cu and Cr concentration profiles in the two re-circulating solutions (anolyte and catholyte) was found in all cases studied (Figs. 5–10). The fastest Cu and Cr appearance rates and, thus, their highest accumulation in the solutions occurred during the early stage of the processes (up to days 4–5), until when the ion fluxes could still

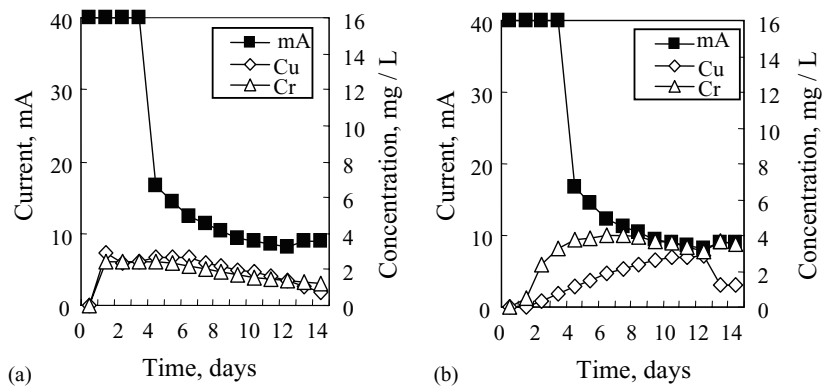


Fig. 5. Dynamics of Cu and Cr accumulation in the re-circulating solutions in the experiment with oxalic acid as the extracting solution under electro-dialytic conditions: (a) Cu, Cr in the anolyte; (b) Cu, Cr in the catholyte.

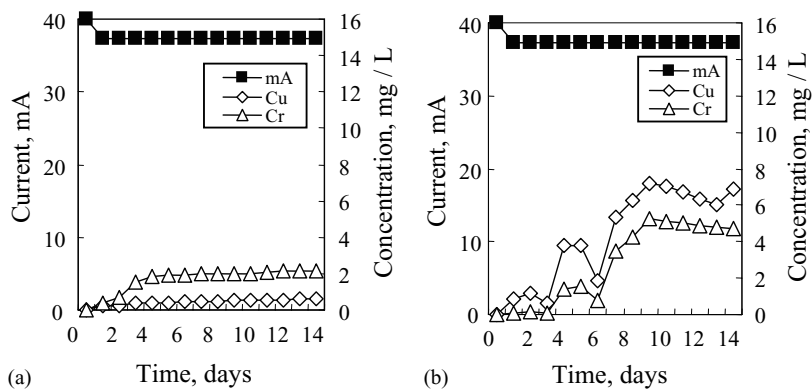


Fig. 6. Dynamics of Cu and Cr accumulation in the re-circulating solutions in the experiment with formic acid as the extracting solution under electrodynamic conditions: (a) Cu, Cr in the anolyte; (b) Cu, Cr in the catholyte.

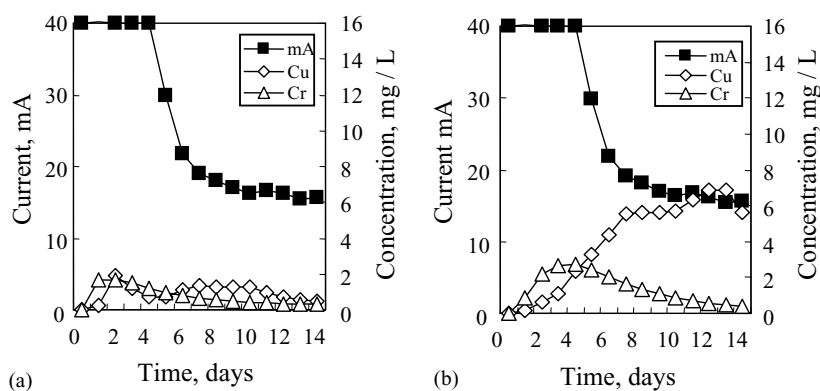


Fig. 7. Dynamics of Cu and Cr accumulation in the re-circulating solutions in the experiment with a mixture of oxalic and formic acid as the extracting solution under electrodynamic conditions: (a) Cu, Cr in the anolyte; (b) Cu, Cr in the catholyte.

support the direct current value of 40 mA imposed initially. This could be attributed to the initial availability of these elements (as cations and/or their complexes with dissociated ions of the organic acids applied) serving as electric current carriers in the beginning of operation. Later on, depletion of current carriers from the wood chips and increased ohmic resistance of the ion exchange membranes could both contribute to the lower possible current values in the ED cell.

The total concentration of Cu and Cr in the catholyte in Experiment FA, performed with formic acid as the extracting solution (Fig. 6b), was higher compared to other acidic extracting solutions (Experiment OA and Experiment OA+FA, Figs. 5b and 7b, respectively). This highest concentration of Cu in the catholyte corresponded to its lowest retention in the cation-exchange membrane (0.11 mg of Cu) and, hence, low membrane resistance. Most probably, the fluxes of Cu

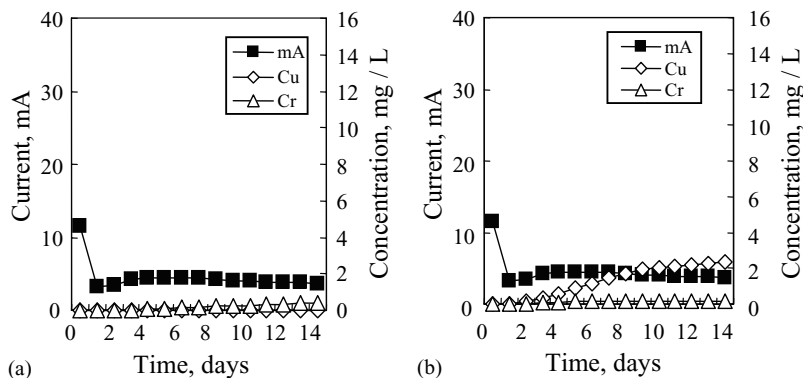


Fig. 8. Dynamics of Cu and Cr accumulation in the re-circulating solutions in the experiment with deionised water as the extracting solution under electrodynamic conditions: (a) Cu, Cr in the anolyte; (b) Cu, Cr in the catholyte.

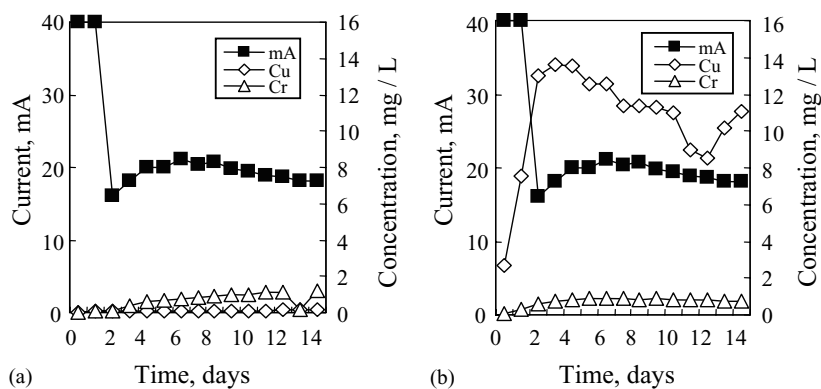


Fig. 9. Dynamics of Cu and Cr accumulation in the re-circulating solutions in the experiment with NaCl solution as the extracting solution under electrodynamic conditions: (a) Cu, Cr in the anolyte; (b) Cu, Cr in the catholyte.

and Cr, when organic acids were used, depend not only on the charges of the complexes formed but also on the size and shape of these complexes since their transport may be hindered by the ion exchange membranes before entering the anolyte and/or catholyte solutions, respectively.

Electrodialytic experiments were also performed with pure deionised water, as well as NaCl and EDTA aqueous solutions as extracting media. Experiment DW was performed with deionised water (similar to Experiment DW (d)), but followed by electrodynamic instead of dialytic treatment. Deionised water was chosen as a control extracting solution because of its very low conductivity (0.001 mS cm^{-1} , Table 1). As expected, the lowest concentrations of target elements were found in the two re-circulating electrolyte solutions (anolyte and catholyte) of this experiment (Fig. 8a and b). Nevertheless, only around 31% of Cu remained in the chips at the end of the experiment, showing its good water solubility and re-mobilisation. Moreover, the maximum Cu concentration found in the catholyte of this experiment, was almost two orders of magnitude higher, than that in the anolyte (0.03 and $2.34 \text{ mg Cu l}^{-1}$, correspondingly). Also, a very high retention of Cu (36.8 mg of Cu) in the cation exchange membrane was found, that is the highest value in comparison with all other experiments. As the pH

value in the central cell compartment was around 5.6–6.0, formation of metal hydroxides of low solubility at this membrane—solution interface is possible [31]. Several detailed investigations of the possible chemical forms of Cr and their behaviour in soils and other geological substances [32], demonstrated formation of species such as Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$ or $\text{Cr}(\text{OH})_3$, when the solution pH is around 6. The tendency of Cu and Cr to form hydroxides could be the reason for the high resistance of ED cell and faster decrease of current when water was used as the extracting solution (Fig. 8).

The behaviour of the system, under conditions when a NaCl solution was applied for wood chips pre-incubation is especially interesting for getting an idea about the possible mechanism of Cu and Cr removal under electrodynamic conditions. It can be clearly seen in Fig. 9b that Cu, as in the case of deionised water, is directed towards the catholyte. The latter means that this element, in both cases, is present as cations (Cu^+ and/or Cu^{2+}) migrating to the cathode. The higher rate of Cu removal in the case of NaCl as the extracting solution (compared to deionised water) might be possibly related to some ion exchange reactions between Na^+ and Cu^+ (Cu^{2+}) containing sites in the CCA-treated material. To confirm this hypothesis, further work is, however, needed. Regarding the removal of Cr, rather low but

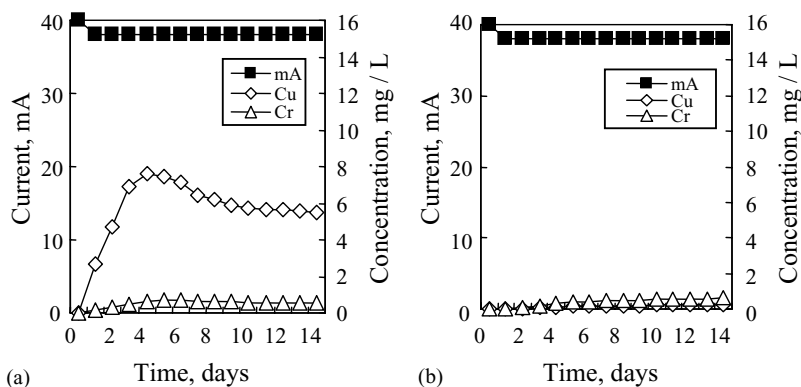


Fig. 10. Dynamics of Cu and Cr accumulation in the re-circulating solutions in the experiment with EDTA as the extracting solution under electrodynamic conditions: (a) Cu, Cr in the anolyte; (b) Cu, Cr in the catholyte.

Table 2
Integral mass balances of Cu and Cr (mg)

Element	Initial total amount	Experiment	Extracting solution	Anode compartment				Cathode compartment				In chips after experiment	Final total amount
				AN ^a	Anolyte	Anode	Total	CAT ^b	Catholyte	Cathode	Total		
Cu	67.2 ± 2.8	DW	1.7	0.1	0.0	1.0	1.1	36.8	2.1	0.0	38.9	19.7	61.4
		DW (d)	1.7	0.2	0.1	0.0	0.3	3.7	0.2	0.0	3.9	53.6	59.5
		NaCl	6.2	0.1	0.1	0.1	0.3	21.4	13.9	10.1	45.4	3.7	55.6
		OA	16.6	4.0	1.1	0.0	5.1	23.6	1.3	4.2	29.1	13.1	63.9
		OA (d)	16.6	5.0	3.7	0.0	8.7	1.2	0.3	0.0	1.5	36.8	63.6
		FA	50.3	0.1	0.6	0.0	0.7	0.1	11.5	4.7	16.3	5.3	72.6
		OA + FA	13.8	4.2	0.6	0.0	4.8	14.8	4.3	9.4	28.5	15.3	62.4
		OA + FA (d)	13.8	4.6	5.0	0.0	9.6	1.5	1.1	0.0	2.6	30.4	56.4
		EDTA	53.0	4.7	5.6	0.0	10.3	0.4	0.2	0.3	0.9	13.1	77.3
Cr	59.6 ± 3.4	DW	0.6	1.0	0.3	0.0	1.3	0.2	0.2	0.0	0.4	59.2	61.5
		DW (d)	0.6	0.2	0.1	0.0	0.3	0.2	0.1	0.0	0.3	54.8	56.0
		NaCl	0.7	0.8	1.0	0.0	1.8	0.9	0.8	1.4	3.1	47.9	53.5
		OA	33.8	7.4	1.4	0.0	8.8	3.4	3.4	1.7	8.5	7.5	58.6
		OA (d)	33.8	13.5	3.7	0.0	17.2	2.5	0.6	0.0	3.1	16.7	70.8
		FA	13.9	0.5	2.1	0.0	2.6	0.8	11.2	0.8	12.8	33.5	62.8
		OA + FA	42.7	10.7	0.5	0.0	11.2	1.3	0.8	3.3	5.4	5.7	65.0
		OA + FA (d)	42.7	11.0	0.5	0.0	11.5	0.6	0.3	0.0	0.9	21.2	76.3
		EDTA	2.5	1.3	0.5	0.0	1.8	3.1	0.5	0.3	3.9	53.0	61.2

^a Anion-exchange membrane.

^b Cation-exchange membrane.

approximately equal transport rates to both anolyte and catholyte solutions were observed. It might be speculated that the CCA-treated wood chips already contained some negatively charged Cr-containing species, which were directed to the anolyte solution under electro-dialytic conditions. The latter rate, however, is quite slow to draw out a definite conclusion. In any case, both water and NaCl solutions, while effective to a certain degree for Cu removal, were found to be not suitable for remediation of Cr.

The final extracting solution examined in this study was EDTA, which is known as one of the most powerful metal extractants. The reason of choosing EDTA as a extracting solution was twofold: first, to assess the efficiency of the two elements removal under such conditions; and, second, to gain more insight into the charge of the possible metal-containing forms when the complex formation is the dominant mechanism. The importance of the latter aspect is clearly shown in Fig. 10a. As it can be seen, contrary to the cases of water and NaCl as extracting solutions, when EDTA was applied practically the whole amount of Cu available in the central wood chips-containing compartment was directed through the anion exchange membrane to the anolyte solution. This means that EDTA shows the highest complex formation affinity towards Cu. Such Cu-containing negatively charged species are expected to form also when organic acids with a lower number of carboxyl groups are used. The direction of Cu removal flow towards anolyte solution could be explained by formation of stable complexes like MeEDTA^{2-} with Me^{2+} ions. Indeed, it was found [31], that for pH values above 2, Cu is present mostly in the complex form Cu-EDTA^{2-} (95%). As expected, oxalic acid is the second (after EDTA) best choice for Cu transport to the anolyte solution (Fig. 5a).

However, the Cu-complex formation power of oxalic acid was not so strong in order to prevent the flux of Cu cations to the catholyte solution (Fig. 5b). On the other hand, EDTA was found to be less effective than oxalic and formic acids for removal of Cr (Fig. 10). Similarly, low Cr removal with EDTA from glacial till—less than 2% was reported [32]. These authors supposed that Cr in glacial till was initially present as precipitate, thus preventing Cr to complex with EDTA. The log stability constant of Cr(III) and OH^- is 47.8, while the log stability constant of Cr(III) and EDTA is 32.2; therefore, EDTA may not be effective in forming complexes with Cr(III) [33]. EDTA was recently tested as an extracting solution for Cu and Cr removal from CCA-treated wood chips and removal efficiencies of 60% for Cu and 13% for Cr have been reported [34]. This behaviour of EDTA is similar to what we have observed and confirms the lower efficiency of this extracting agent for removing Cr from the CCA-treated wood.

3.4. Effect of the extracting solution on the overall removal efficiencies for Cu and Cr

In order to assure that the system operated properly, Cu and Cr integral mass balances were checked over the time

Table 3

Overall removal efficiencies^a of the target elements from the wood chips (%)

Experiment	Cu (%)	Cr (%)
DW	70.7	0.7
DW (d)	20.2	8.1
NaCl	94.5	19.6
OA	80.5	87.4
OA (d)	45.2	72.0
FA	92.1	43.8
OA + FA	77.2	90.4
OA + FA (d)	54.8	64.4
EDTA	80.5	11.1

^a Overall removal efficiency = ((element amount (mg) in the chips before treatment – element amount (mg) in the chips after treatment)/element amount (mg) in the chips before treatment) × 100%.

duration of the experiments before calculating the removal efficiencies. The balances between the initial amount and final distribution of the element under study for all the experiments performed are summarised in Table 2. As can be seen the general requirement of mass conservation is satisfied reasonably well by comparing the second and the last column of Table 2.

The overall removal efficiencies for Cu and Cr as a function of the type of extracting solution are summarised in Table 3. As it can be seen from the data obtained, oxalic acid proved to efficiently solubilise (extract) the target elements from CCA-treated wood waste. Moreover, it can be partially replaced by formic acid since the removal efficiencies were close to the case when oxalic acid was the single extracting agent. The latter points out the potential of using mixtures of different organic acids and opens different possibilities to design the composition of the extracting solution depending on the elements and their desired removal efficiencies. If Cu removal is of primary concern, NaCl solutions of relatively low salinity (1.25% (w/v) in the case studied) or even water alone could be used as extracting media.

4. Conclusions

The results obtained show the important role of the type of extracting solution for the subsequent electro-dialytic removal of heavy metals from CCA-treated wood waste. The extracting solution has a strong impact on both magnitude and direction of the target element fluxes under electro-dialytic conditions, therefore, its proper selection is crucial for the overall process performance.

Individual organic acids, such as oxalic or formic acid, were found to support the efficient removal of both Cu and Cr from CCA-treated wood waste. The use of mixtures of individual organic acids is possible, however, it does not improve the overall removal efficiency. If these acids are used as extracting solutions under electro-dialytic conditions, Cu and Cr removal from the wood chips as positively as well as negatively charged compounds occur, so,

the elements are accumulated in both catholyte and anolyte solutions.

NaCl extracting solution was found suitable for Cu removal but ineffective for Cr solubilisation and removal from CCA-treated wood chips. In this case, Cu was almost entirely accumulated in the cathode compartment due to its presence in a cationic form. If cathode reduction recovery of Cu for its possible re-use is desired, these conditions will be superior, compared to the situations of organic acids as extracting solutions, because, in the latter cases, part of Cu is directed to the anode compartment.

The good complex formation power of EDTA towards Cu was confirmed and, under such conditions, the flux of Cu was entirely to the anode compartment since less or no free Cu cations were available. However, the removal efficiency for Cr was rather low in this case. Therefore, the use of oxalic or formic acid is more appropriate when the removal of both elements, Cu and Cr, from wood waste is desired.

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