



## A comparative study on Cu, Cr and As removal from CCA-treated wood waste by dialytic and electro-dialytic processes

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### Abstract

In this study, electro-dialytic and dialytic techniques were used for Cu, Cr and As removal from 20-years out-of-service CCA-treated *Pinus pinaster* Ait. pole. The effect of applying direct current, as “cleaning agent”, of up to 120 mA was investigated. Focus was given to a parallel comparison with the performance of a pure dialytic experiment (without an external power supply) in order to reveal transport of charged particles induced solely by internal electrochemical potential differences in the system. Oxalic acid proved to be a more suitable pre-treatment solution than deionised water for wood chips incubation. Evaluation of the IARs of Cu, Cr and As showed that the rates of their appearance in the electrolytes were not linearly related to the current (except for Cr in the catholyte), mainly because of membrane retention. The maximum removal efficiencies obtained in a batch electro-dialytic cell operated for 14 days were as follows: Cu, 84%; Cr, 87%; and As, 95%. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Heavy metals; Solid waste; Electro-dialysis; Electrokinetic remediation

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### 1. Introduction

The most common formulation, which has been used to preserve wood from insects, fungi and water damage by impregnation, is the solution of copper, chromium and arsenic salts, known as chromated copper arsenate (CCA). Recent reports reveal increasing amounts of CCA-treated wood waste in- or out-of-service. For instance, in France, about 25 million CCA-treated poles are in service; in Germany, the annual impregnated production is

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approximately 3.3–4.7 million m<sup>3</sup> [1,2]. The annual production of CCA-treated wood products in the USA in the 1970s has been over 5 million metric tonnes, and it is estimated that over 85 million metric tonnes of this product is in service [3]. Based on the average service life of 20–50 years (in case of decks, up to 9 years [4]), it is expected that this amount of CCA-treated wood is now being, or will soon be, removed from service, which raises an environmental issue of how to deal with this wood waste management problem.

Both legislation and drawbacks of the traditional disposal method (land-filling) is motivating studies of alternatives for recycling and reuse of CCA-treated wood waste. As feasibility options, re-use of decking material in construction projects, and/or removal of the preservatives and using the remaining wood fibres to manufacture composite wood products have been suggested [4,5].

The incineration, followed by recovering the metals from ashes [6] is another approach for utilisation of CCA-treated timber waste. A low temperature pyrolysis processing [1,7,8] is suggested as an alternative method, preventing highly toxic smoke and fumes emissions to the environment in result of incineration [9]. However, pyrolysis leads to a total destruction of the treated wood and a highly rich of Cu, Cr and As solid residue, that has to be further manipulated.

There are some biological [10–12] and biochemical [13,14] purification methods, which have shown encouraging laboratory results regarding the removal efficiencies of Cu, Cr and As. However, the suitability of biological processes for CCA-treated wood purification seems to be limited for a large-scale application [11,15] because the CCA accumulating fungus growth can be totally inhibited by other organisms, not accumulating the target metals. Obviously, sterilisation of the wood and maintaining aseptic conditions in a large-scale would be impossible for economic reasons.

In our study, a fundamental phenomenon, the movement of charged particles in an electrical field, was applied to a new object, CCA-treated chipped wood waste, to assist Cu, Cr and As removal. It is known that electrodialysis is chiefly used for brackish water desalination and pre-concentration of sea-water for salt production [16], where it has proved to be an economic solution for many years; however, new applications have been tested in different industries. Recently, besides the already suggested electrodialytic method for heavy metal soil remediation [17–19], a study on the potential of the electrodialytic process for remediation of CCA-treated timber waste, in the form of sawdust, has been initiated [20].

The high efficiency of the electrodialytic technique is based on the movement of the charged particles towards electrode compartments (electrodes and electrolyte solutions), if an external potential difference is applied between the electrodes, from where they may be easily removed. The advantages of the electrodialytic technique for removal of metals from CCA-treated wood waste may be summarised as follows:

- (i) a low-level direct current can be used as a “cleaning agent”,
- (ii) ion-exchange membranes allow regulating the direction and magnitude of the ion fluxes,
- (iii) the metal removal degree can be controlled by adjusting the flow rates of the solutions contacting the membranes,
- (iv) the metals (Cu, Cr and As) removed might be re-used,
- (v) the “cleaned” timber waste might be further recycled.

Special attention, in the present study, was given to the effect of current strength on Cu, Cr, and As removal from CCA-treated timber waste using wood chips. The latter are more realistic compared to sawdust, since less energy is spent for their preparation and the health risk is much lower. Furthermore, a comparison was done with a “pure” dialytic treatment of wood chips, incorporating ion-exchange membranes, under identical conditions, except for the absence of an external power supply. The dialytic studies were carried out to get a better insight into the transport mechanism of free ions (contaminants) that, under such conditions, is governed solely by internal electrochemical potential differences in the system.

## 2. Material and methods

### 2.1. Polluted material

Wood chips, prepared from 20-years out-of-service CCA-treated *Pinus pinaster* Ait. pole, were used in the experiments. These chips had the following dimensions: length 10–15 mm, width 2–10 mm, thickness 1 mm, and contained a fraction of around 10% as a fine powder. The total target metal contents in the timber waste, in  $\text{g kg}^{-1}$ , were: Cu, 1.68 ( $\pm 0.07$ ); Cr, 1.49 ( $\pm 0.08$ ); and As, 1.95 ( $\pm 0.01$ ); as determined according to Method 1 of the British Standard [21].

### 2.2. Laboratory cell

All experiments were run for 14 days in a batch laboratory electro dialytic cell. The principle configuration of this type of cell was developed at the Technical University of Denmark [22] and is described in detail elsewhere [18,19]. The electro dialytic cell consists of three compartments—two electrode compartments and a central compartment separated by two ion-exchange membranes: a cation-exchange membrane (CAT) IC1-61CZL386 and an anion-exchange membrane (AN) IA1-204SXZL386, both supplied from Ionics Inc., USA (Fig. 1). The central compartment, where wood chips were placed, had a length

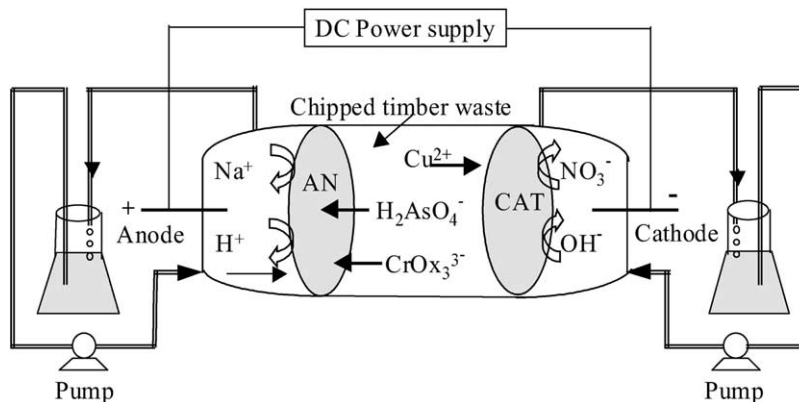


Fig. 1. Schematic diagram of the electro dialytic (ED) cell.

Table 1  
Experimental conditions<sup>a</sup>

Experiment	Initial current (mA)	Assisting agent (pre-treatment incubation)
1	11.6 <sup>b</sup>	Deionised water
2	0.0	Oxalic acid (2.5%)
3	40.0	Oxalic acid (2.5%)
4	60.0	Oxalic acid (2.5%)
5	120.0	Oxalic acid (2.5%)

<sup>a</sup> After static incubation (24 h) of 40 g of wood chips in the “assisting agent” (deionised water or oxalic acid) in a liquid/solid phase ratio of 8.8 (w/w).

<sup>b</sup> A maximum possible value obtained in the system.

of 3 cm and an internal diameter of 8 cm. Through each electrode compartment, 1 l of  $10^{-2}$  M  $\text{NaNO}_3$  solution circulates in a closed system. Constant flow rates of  $0.61 \text{ h}^{-1}$  to both electrode compartments were maintained by a multichannel peristaltic pump (Watson Marlow 503 U/R, USA). The pH value of the catholyte solution was adjusted to about 3 by periodical addition of concentrated  $\text{HNO}_3$ . The electrodes were platinised titanium bars with a diameter of 3 mm and length of 5 cm (Bergsøe Anti Corrosion A/S, Denmark). A power supply (Hewlett Packard E3612A, USA) was used to adjust the desired initial direct current (DC) monitored by a Fluke 37 multimeter. Five experiments were carried out for 14 days under the experimental conditions listed in Table 1.

### 2.3. Analytical methods

During each experiment, samples of the electrolyte solutions (catholyte and anolyte) were collected and analysed for Cu, Cr and As. At the end of each experiment, the concentration of these target metals in the ion-exchange membranes was determined in the filtrates (after immersing each membrane for 48 h in 1 M HCl solution). Metals deposited on the electrodes were analysed in solutions, obtained after immersing each electrode in 1 M HCl solution and applying a potential reversal against a clean electrode. The final “total” amount of each element in the wood chips after the experiments was also analysed according Method 1 of the British Standard [21]. Cu and Cr were determined by atomic absorption spectrometry (Perkin-Elmer 300-AAS), and As by inductively coupled plasma (ISA Jobin-Yvon 24-ICP).

## 3. Results and discussion

The current in electrodialysis is presented by ion fluxes in the system, under the influence of an externally applied electric potential difference [16]. In the electro-dialytic removal techniques, the flux of ions is composed of charged particles, including contaminants and/or their complexes, which move in an electric field ( $E$ ) to the corresponding electrodes, according to their charge ( $z$ ). The individual ion velocity ( $v_i$ ) is proportional to the electric field strength:

$$v_i = u_i z F E, \quad (1)$$

where  $u_i$  is the ion mobility and  $F$  is the Faraday constant.

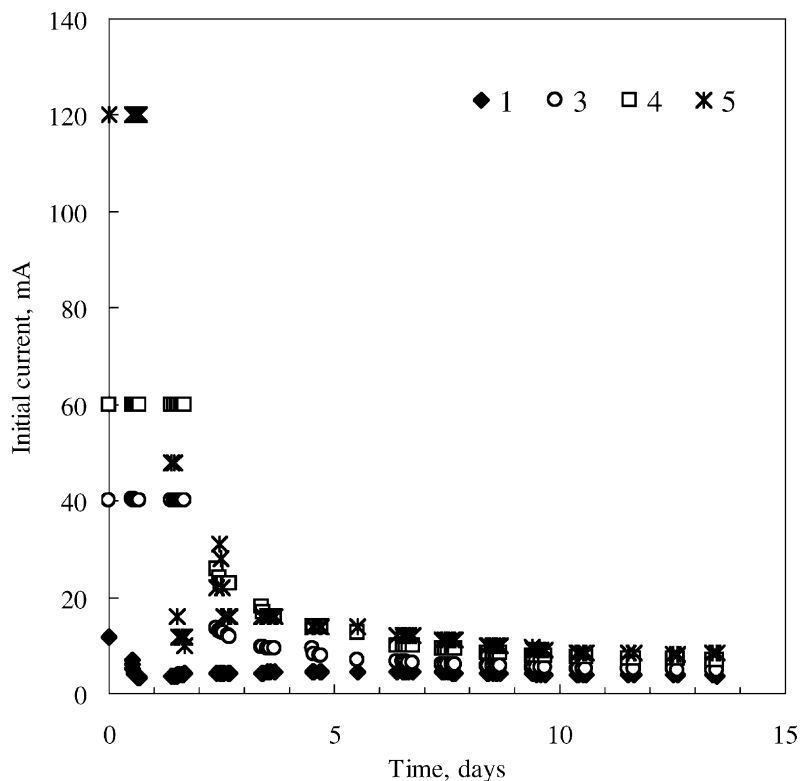


Fig. 2. Time course profiles of the values of direct current passing through the electroalytic cell during the experiments. The initial current values for the experiments were as follows: experiment 1, 11.6 mA; experiment 3, 40 mA; experiment 4, 60 mA; and experiment 5, 120 mA. Experiment 2 was performed without an external power supply.

The time course values of the current, passing through the electroalytic cell studied, showed a relative stability in the beginning of the experiments, followed by a decrease in the later stages (Fig. 2). As expected, at lower initial current strength (40 and 60 mA), the overall cell conductivity could be kept for longer time (around 2 days). The highest initially passing current of 120 mA, kept its constant value during only the first day of operation and then dropped sharply. At higher initial current, due to accelerated electromigration, the depletion of charged particles in the treated timber waste should occur faster (Eq. (1)). The data for the electroalytic cell resistance, calculated 1 day after the start-up of the experiments, are presented in Table 2. It can be seen that a very high resistance value was reached for experiment 1. Therefore, the electroalytic system in this experiment, in which pre-treatment incubation with deionised water (conductivity of less than  $10^{-3}$  mS  $\text{cm}^{-1}$  at  $25^\circ\text{C}$ ) was performed, could not achieve an initial current value higher than 11.6 mA. This low value dropped further to 3.5 mA after 1 day of operation. These results show the important role of 2.5% oxalic acid solution (conductivity of  $25.5$  mS  $\text{cm}^{-1}$  at  $25^\circ\text{C}$ , experimentally determined) as an “assisting” agent for the contaminants mobilisation, and

Table 2  
Electrolytic cell parameters at the start of the experiments ( $t = 0$  h) and after 24 h of operation

	Time (h)							
	0 (experiment 1)	24 (experiment 1)	0 (experiment 3)	24 (experiment 3)	0 (experiment 4)	24 (experiment 4)	0 (experiment 5)	24 (experiment 5)
Current (mA)	11.6	3.5	40.0	40.0	60.0	60.0	120.0	48.0
Voltage (V)	82.6	87.5	16.0	12.5	25.3	63.3	61.9	137.8
Resistance (k $\Omega$ )	7.1	25.0	0.4	0.3	0.4	1.1	0.5	2.9

as an electric current carrier in the system. As in our previous work [20], oxalic acid proved to be suitable for Cu, Cr and As removal from CCA-treated wood.

At initial current strength of 40 mA, the experimental data showed a slight decrease of the electrical potential difference and resistance after 1 day of operation. Probably, under these experimental conditions, there were still enough available charge particles (contaminant cations and/or their complexes with dissociated ions of oxalic acid) [20] present in the electro-dialytic cell central compartment. Six days after the start of the experiments with initial current of 11.6, 40, 60 and 120 mA, the electric current became nearly constant and equal to 4.5, 6, 10 and 12 mA, respectively (Fig. 2). The higher current values at higher potential differences applied may be attributed to enhanced water dissociation at the electrodes under such conditions [23].

The initial accumulation rate (IAR) of the metals in the electrolytes were calculated from the individual metal concentration differences in each electrolyte ( $\Delta C_i$ ) for the first 24 h operation. During this initial period, the removal processes can be directly related to the magnitude of the passing current, which kept constant values, according to the following equation:

$$\text{IAR}_i = \frac{\Delta C_i}{\Delta t}, \quad (2)$$

where  $\Delta C_i = C_i - C_0$ , and  $\Delta t = 24$  h.

In general, our data showed significantly higher IARs of the investigated elements in the experiments with an external power supply (Table 3). The IARs of the metals for the anolytes (except for the initial Cr-IAR at 120 mA) were always dominant and higher than those for the catholytes, especially in the experiments with an external power supply. This behaviour may be attributed to initially available Cu and Cr negatively charged oxalate complexes, as well as negatively charged As compounds (such as  $\text{H}_2\text{AsO}_4^-$ ) in the wood chips, formed during the pre-treatment incubation procedure with oxalic acid. In the dialytic experiment 2 (no external power supply), the driving forces, which can lead to fluxes of charged components, are only concentration gradients and internal electric potential differences in the electro-dialytic cell. The initial concentration of elements, which have to be removed from the chips in the central compartment, depend on the desorption processes, assisted by the oxalic acid pre-incubation. As the electrochemical potential of ions (contaminants) on both sides of the ion-exchange membranes is different, internal ion fluxes are generated in the system. Therefore, the movement of charged components to the two compartments, without

Table 3  
Initial metal accumulation rates in the electrolytes ( $\text{mg l}^{-1} \text{ h}^{-1}$ )

Experiment	Cu		Cr		As	
	Anolyte	Catholyte	Anolyte	Catholyte	Anolyte	Catholyte
1	0.001	0.002	0.000	0.000	0.101	0.005
2	0.049	0.006	0.042	0.001	0.139	0.024
3	0.123	0.001	0.102	0.020	0.649	0.017
4	0.073	0.004	0.088	0.045	0.500	0.002
5	0.070	0.010	0.033	0.107	0.490	0.033

an external power supply, is limited by the ion mass transport through the membranes and diffusion boundary layers, contacting the membranes.

The lowest IARs in all experiments were found for Cu, especially for the catholyte, in the dialytic experiment. A potential–pH equilibrium diagram for the system copper–water [24] shows that, under acidic conditions, Cu exists mainly as positively charged ions, which are expected to move through the cation-exchange membrane. This diagram, however, describes an ideal system and does not take into account possible dissolution and precipitation processes. The retarded Cu-IAR in the catholytes may be due to the presence of complex compounds between the CCA-preservatives and wood, as well as between Cu/Cr and Cu/As species. Such compounds have been indeed identified and discussed by Pizzi [25]. The higher thickness of the cation-exchange membrane used in our study and possible membrane poisoning by organic anions [16] causing an increase in the corresponding membrane resistance could also contribute to the lower Cu-IAR values found for the catholytes. Increased Cu-IAR values were observed for the anolytes when direct current of 40 and 60 mA was passing through the electro-dialytic cell (Table 3). However, the dependence of Cu-IAR on the current at higher values (120 mA) was non-linear, probably because of faster anode reactions. It may be suggested that  $\text{Cu}^{2+}$  ions would prevail in the central compartment of the electro-dialytic cell after the depletion of oxalate anions, which readily form Cu complexes, as already discussed. Probably, at the beginning, copper mobilisation is linked to formation of oxides, hydroxides, organic polyanions and anionic complexes due to oxalic acid dissociation. These results agree well with the data of other authors [11,15].

There was a clear relationship between the current and Cr-IAR values obtained for the catholytes (Table 3). At 40, 60 and 120 mA, the Cr-IAR values in the catholytes reached values of 0.020, 0.045 and 0.107  $\text{mg Cr l}^{-1} \text{h}^{-1}$ , respectively. The positively charged  $\text{Cr}^{3+}$  ions and their complexes with oxalate [24] seem to be mobilised faster and easily from the treated wood chips. In the dialytic experiment, the Cr-IAR of 0.042  $\text{mg Cr l}^{-1} \text{h}^{-1}$  was found for the anolyte, whereas in the catholyte, this value was more than an order of magnitude lower—0.001  $\text{mg Cr l}^{-1} \text{h}^{-1}$  (experiment 2, Table 3). Thus, our data clearly demonstrate the important role of applying current to increase the Cr-IAR in the electrolytes. In the anolytes, the Cr-IAR values, when DC of 40 or 60 mA was applied (experiments 3 and 4), exceeded more than two times those in the dialytic experiment and reached 0.102 and 0.088  $\text{mg Cr l}^{-1} \text{h}^{-1}$ , respectively. As discussed by Vallejo et al. [26], the electrotransport of  $\text{Cr}^{6+}$  oxo-anions through an anion-exchange membrane is a function of the  $\text{CrO}_3$  concentration and pH on both sides of the membrane. This transport strongly depends on the polychromate ion formation within the membrane, which is favoured by both the high concentration compared to that in the bulk solution and the proton leakage usually encountered when an ion-exchange membrane is in contact with acidic solutions. Experimental evidence, supporting the presence of Cr-oxalate complexes in the anion-exchange membrane used in our experiments, was the visually detected change of membrane colour, from white to violet, 1 day after the experimental start-up. Such a violet colour has been attributed to the complexation reaction of chromium with oxalic acid [11]. At the highest current of 120 mA, the rate of accumulation of Cr in the catholyte became higher because lower retention of this metal (compared to that of Cu) in the cation-exchange membrane was observed (Table 3). The Cr-IAR in electrolytes was essentially 0 in experiment 1, performed with wood chips



incubated with deionised water. The strong chemical bounds of CCA-preservatives with the wood fibres [25] and their fixation mechanism [27] is based on Cr precipitation compounds, which are slightly water-soluble.

Comparing As-IAR in electrolytes with the previously discussed ones (Cu-IAR and Cr-IAR), it can be seen that these values are about an order of magnitude higher (Table 3). This tendency was kept for both—dialytic and electro-dialytic experiments. The relatively high As-IAR values for the dialytic experiment might be associated with faster mobilisation/desorption processes of As during incubation with oxalic acid. The availability of negatively charged As compounds in the central electro-dialytic cell compartment would facilitate the mobilisation of this element. It has been indeed established, that in aqueous solutions, the forms of arsenic acid that should be thermodynamically more favourable at pH about 2 (encountered in our study) is  $\text{H}_2\text{AsO}_4^-$  [28].

The effect of initial current on the time course of the target metal concentrations in the electrolytes was studied. The corresponding concentrations of the target metals in the two electrolyte solutions are presented in Fig. 3. Pronounced differences in the kinetics of the individual element accumulation processes were observed under conditions without an external power supply, especially for the catholyte solution. In this case, Cu, Cr and As moved preferentially towards the anolyte solution (Fig. 3a, c and e). For Cr, and particularly for Cu, this may be associated with formation of their negatively charged oxalate complexes in the central compartment. Therefore, the final distribution of the elements between the two electrolyte solutions in the electro-dialytic cell was significantly affected (Table 4). Copper accumulation in the catholyte under conditions of no external power supply (experiment 2) showed the lowest values and reached a maximum of only  $0.32 \text{ mg Cu l}^{-1}$  (Fig. 3b). This behaviour led to accumulation of a six times higher amount of Cu in the “anode compartment” (anode, anolyte, anion-exchange membrane) compared to the “cathode compartment” (cathode, catholyte, cation-exchange membrane) (Table 4). Our results also showed that the concentration of Cu in the anolytes in the experiments with an external power supply could be attributed to the pre-treatment incubation of the wood chips with oxalic acid. When water was used instead of oxalic acid for chips pre-incubation (experiment 1) a very low concentration was detected in the anolyte— $0.03 \text{ mg Cu l}^{-1}$  (Fig. 3a), whereas in the catholyte this concentration was similar to those, found in the experiments with current (Fig. 3b). As expected, the application of an external driving force (electric potential difference between the electrodes) results in a strong stimulation of the movement of  $\text{Cu}^{2+}$  cations to the “cathode compartment” of the electro-dialytic cell. At a current of 40 mA, the “cathode compartment” contained six times higher amount of Cu compared to that in the “anode compartment” (Table 4). The enhanced contribution of the electrode reactions is clearly demonstrated at higher current values (120 mA). Under such conditions, the retention of Cu in the cation-exchange membrane was partially overcome and higher amounts of copper moved to the “anode compartment” of the electro-dialytic cell. Therefore, the final distribution ratio of copper between the two electro-dialytic sides (“cathode compartment”/“anode compartment”) decreased to about 2. In all cases, lag time periods were found to be required for the appearance of copper in the electrolytes, being longer for the catholytes. Higher amounts of this element were retained in/on the cation-exchange membranes, compared to the anion-exchange membrane and also to the other target elements (Table 4). Furthermore, voltage drop data obtained recently for the various parts of

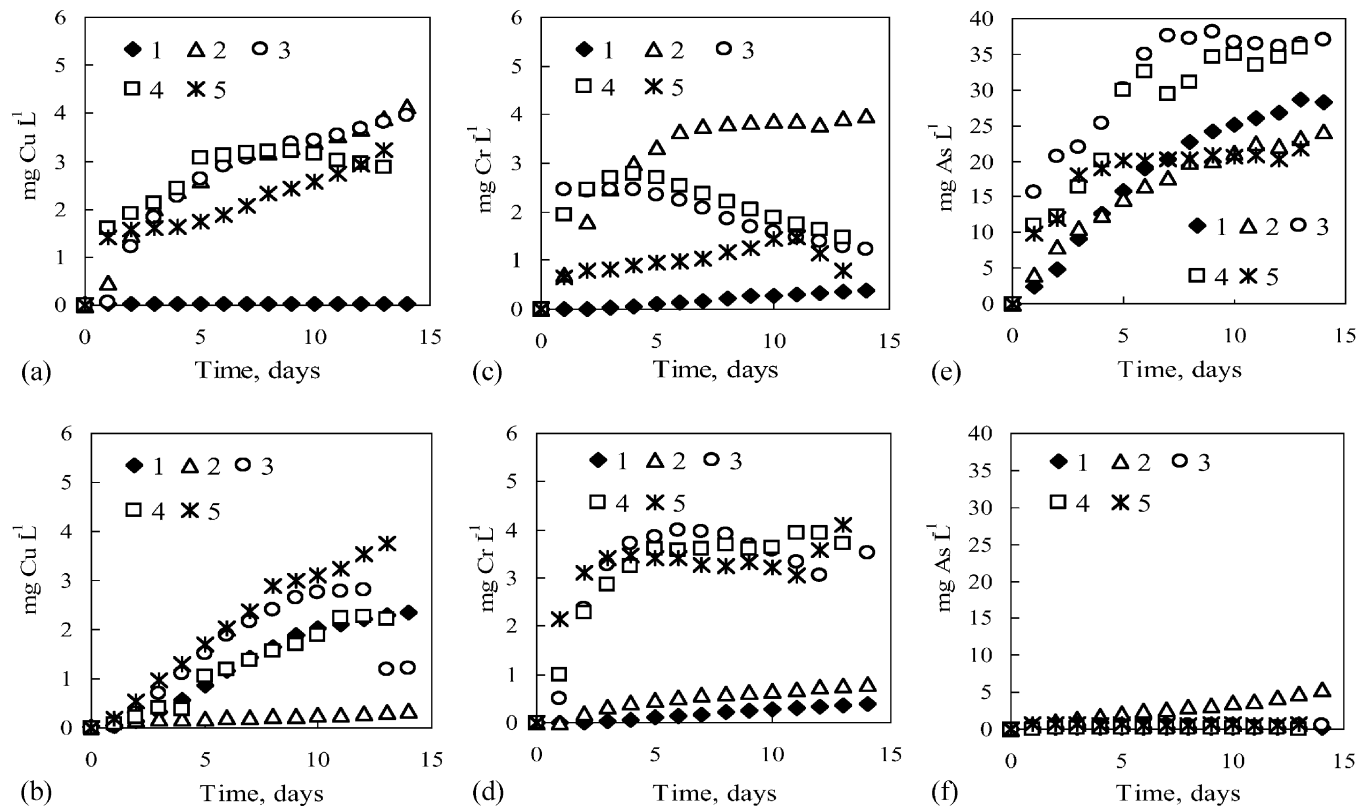


Fig. 3. Time course of Cu, Cr and As concentrations in the electrolyte solutions (a, c and e for the anolyte and b, d and f for the catholyte). The initial current values for the experiments were as follows: experiment 1, 11.6 mA; experiment 3, 40 mA; experiment 4, 60 mA; and experiment 5, 120 mA. Experiment 2 was performed without an external power supply.

Table 4  
Mass balances of Cu, Cr and As for the experiments (mg)

Element	Initial total amount	Experiment	Pre-treatment solution <sup>a</sup>	Anode compartment				Cathode compartment				In chips after experiment	Final total amount
				AN <sup>b</sup>	Anolyte	Anode	Total	CAT <sup>c</sup>	Catholyte	Cathode	Total		
Cu	63.8 ± 2.7	1	1.7	0.1	0.0	1.0	1.2	36.8	2.1	0.0	38.9	18.7	60.4
		2	16.6	5.0	3.7	0.0	8.7	1.2	0.3	0.0	1.4	34.9	61.7
		3	16.6	4.0	1.1	0.0	5.1	23.6	1.3	4.2	29.1	12.5	63.2
		4	16.6	3.8	2.8	0.0	6.6	24.4	2.0	2.2	28.6	14.7	66.6
		5	16.6	4.5	3.0	5.3	12.7	16.6	3.4	6.7	26.8	10.3	66.3
Cr	56.6 ± 7.4	1	0.6	1.0	0.3	0.1	1.4	0.2	0.2	0.0	0.4	56.2	58.6
		2	33.8	23.5	3.7	0.0	27.2	2.5	0.6	0.0	3.1	15.9	80.0
		3	33.8	17.4	1.4	0.0	18.8	3.4	3.4	1.7	8.5	7.1	68.3
		4	33.8	12.9	1.6	0.0	14.5	6.1	3.6	1.3	10.9	9.7	68.9
		5	33.8	9.7	0.8	2.0	12.5	4.2	3.9	2.5	10.6	11.0	67.9
As	74.1 ± 11.0	1	12.9	0.9	26.1	0.0	27.0	0.2	0.2	0.0	0.4	59.7	100.0
		2	39.4	0.6	21.7	0.0	22.3	0.7	3.9	0.0	4.6	14.4	80.7
		3	39.4	2.1	35.0	0.0	37.1	0.5	0.5	0.1	1.1	3.4	81.0
		4	39.4	1.7	32.9	0.0	34.5	0.3	0.0	0.1	0.4	5.3	79.6
		5	39.4	3.5	21.0	0.3	24.8	0.2	0.6	0.1	1.0	4.9	70.0

<sup>a</sup> A time of 24 h after incubation of chips in the “assisting” agent.

<sup>b</sup> Anion-exchange membrane.

<sup>c</sup> Cation-exchange membrane.

the same type of electrodiolytic cell have shown the appearance of an additional resistance close to the cation-exchange membrane facing the polluted material compartment [29]. This problem was associated with a probable water splitting and subsequent formation of a Cu-hydroxide precipitate layer of high resistance under such conditions.

The Cr concentration kinetic curves reached faster their maximum values, compared with Cu and As (Fig. 3c and d). Similarly to Cu mobilisation in the electrodiolytic cell under conditions without external power supply (experiment 2), Cr mobilisation was dominated by a flux towards the “anolyte”, probably due to formation of negatively charged Cr compounds (oxides and hydroxides [24] or complexes with oxalic acid [30,31]) under acidic conditions. Thus, the Cr accumulation in the “anode compartment” was nine times higher compared to that in the “cathode compartment” under dialytic conditions (Table 4). The relatively high retention of 23.5 mg of Cr by the anion-exchange membrane has to be mentioned. This was probably due to polychromate ion formation that was found for anion-exchange membranes, exposed to a similar condition [26]. The mass balance data for Cr showed a change in the direction of its flux when current was passing through the electrodiolytic cell. The minimum concentration of Cr was found in the electrolytes of experiment 1 (chips pre-incubation in

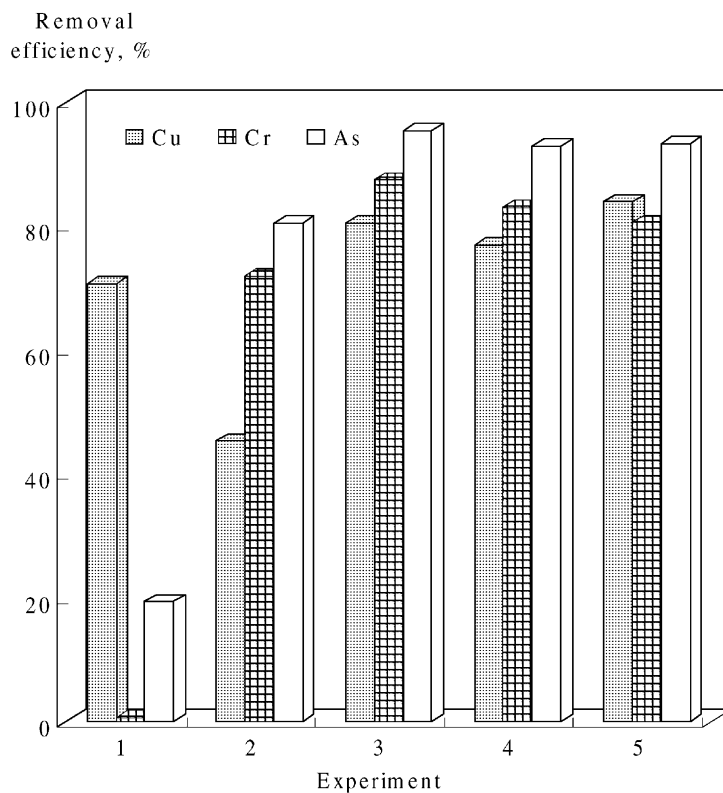


Fig. 4. Comparison of the overall efficiencies of Cu, Cr and As removal from the wood chips as a function of the initial current.

water), as under neutral pH conditions  $\text{Cr}^{3+}$  ions mainly precipitate [23]. The chromium concentration in the catholyte increased significantly by increasing the current in the system (Table 4).

Regarding the time course of arsenic accumulation in the anolyte solutions, the most important difference compared to the cases of Cu and Cr was that the mobilisation of As was obviously independent of oxalate complexes formation. Since As showed a similar kinetic concentration curve when water was used for chips incubation, it may be considered that the presence of negatively charged As oxides and hydroxides was sufficient to support its flux to the anolyte solution. Moreover, the retention of As in the anion-exchange membrane (AN) was negligible (0.6 mg of As). Therefore, its mass balance was almost completely presented by the amount accumulated in the anolyte (Table 4).

Finally, the removal efficiency for Cu was the most strongly influenced by applying an electric current in the range of 40–60 mA, being the highest (84%) at 120 mA (Fig. 4). For Cr and As, the removal efficiencies were similar under all electro-dialytic conditions tested, reaching a maximum of around 80% for Cr and 93% for As. Dialytic conditions were found to be not effective for removing Cr and only slightly effective (about 20% removal) for As.

#### 4. Conclusions

- The applicability of the electro-dialytic technique for removal of Cu, Cr and As from CCA-treated wood was demonstrated for the chipped form of this solid waste.
- The comparison of the electro-dialytic method with a “pure” dialytic treatment helped to understand better the mechanism of the removal processes. Based on this comparison, similarities, but also several peculiarities, were detected.
- The evaluation of the initial rates of Cu, Cr and As accumulation in the electrolytes showed that the rate of appearance of the elements studied was not affected by the magnitude of the current for the anolyte solutions. The general order of appearance in the anolytes was  $\text{As} > \text{Cu} \cong \text{Cr}$ . For the catholyte solutions, the rate of appearance of the elements kept the order  $\text{As} > \text{Cu} \cong \text{Cr}$ , only under conditions without external power supply. This order changed to  $\text{Cr} > \text{As} \cong \text{Cu}$  under electro-dialytic conditions.
- The maximum removal efficiencies in this study were obtained under electro-dialytic conditions, and were as follows: Cu, 84%; Cr, 87%; and As, 95%.

Further improvement of these efficiencies, as well as of the overall performance of the electro-dialytic process may be achieved by optimising the hydrodynamic conditions in the cell compartments and using thinner ion-exchange membranes. The composition and concentration of the wood chips pre-treatment solution also proved to be rather important.

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