Original Paper

Cu and Cd removal from wastewater by a microalloyed aluminium composite

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Abstract We studied the removal of cadmium and copper from industrial wastewaters by a microalloyed aluminium composite. The composite was highly efficient, resulting in water concentrations of cadmium and copper below the maximal allowed concentrations for drinking water. Moreover, our results show that the removal mechanism is mainly based on reduction and coprecipitation, since Cd and Cu were removed from the wastewater in reduced forms as metals and hydroxides.

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Introduction

Cadmium is a naturally occurring metal used in various chemical forms in electroplating, in solder for aluminium, as a constituent of easily fusible alloys, in process engraving, and in cadmium-nickel batteries. Its concentration in wastewaters ranges from 3 to 55 mg L^{-1} (Paterson *1975*). Cadmium is highly toxic to humans and other living organisms. Environmental exposure can occur via diet and drinking water. Acute oral exposure to cadmium may cause

gastrointestinal irritation, vomiting, abdominal pain, and diarrhoea. Longer-term exposure to cadmium primarily affects the kidneys, resulting in tubular proteinosis, although other conditions such as "itai-itai" disease may involve the skeletal system (ATSDR *1989*).

Cadmium is transported in the blood and widely distributed in the body, but accumulates primarily in the liver and kidneys (Goyer *1991*). Metabolic transformations of cadmium are limited to its binding to protein and nonprotein sulfhydryl groups, and various macromolecules, such as metallothionein, which is especially important in the kidneys and liver (Goyer *1991*). In addition, cadmium, like other heavy metals, cannot be degraded in the environment. However, it can react with the environment, and may be bioconcentrated. Usually, the only way to control pollution caused by this metal is wastewater treatment (ATSDR *1989*).

The principal source of copper in industrial waste streams comes from metal cleaning and plating baths, printed circuit board manufacturing baths, and rinses such as wire drawing and copper polishing, which requires periodic oxide removal by immersing the metal in acid baths (Paterson *1975*). Wastewaters usually contain copper in a concentration range from 5 to 120 mg L^{-1}. Copper is not considered very harmful to human health, but at high concentrations in drinking water, copper may cause an unpleasant taste and affect certain individuals suffering from a copper metabolism disorder called Wilson's disease. Excess copper interferes with zinc, a mineral needed to make digestive enzymes, and impairs thyroid activity and the functioning of the liver (Goyer *1991*).

In the goal to clean up wastewaters containing cadmium and copper, many techniques are used such as precipitation as insoluble salts and precipitation as metals and ion exchange (Paterson *1975*). This study investigates a new treatment for the removal of divalent cadmium and copper ions from aqueous solutions by applying a microalloyed aluminium composite. Because of its very negative electropotential in aqueous solutions, the composite behaves as a strong reducing agent and may affect various pollutants in the water (Novaković et al.*1998*b; Bojić et al. *2001*). Additionally, as a final product of the microalloyed aluminium-dissolution in water, the insoluble Al(OH)$_3$ appears, which works to coprecipitate pollutants and their degradation products from the water phase (Novaković et al. *1998*a; Novaković et al. *1998*b, Park et al. *2002*). Previous studies reporting the purification (Novaković et al. *1998*a; Novaković et al. *1998*b) and disinfection (Bojić et al. *2001*) of different waters, show that a microalloyed aluminium composite is not selective. Therefore, different species in the form of ions, molecules, and colloids can be removed with great efficacy. In most cases, the concentrations of pollutants decline several logs in a relatively short period, and often they are below the maximal allowed concentrations for drinking water.

Experimental

The experiments were carried out with industrial wastewaters. In the case of cadmium, the water solution for the microalloyed aluminium composite treatment was supplied by a firm that carries out decorative cadmium plating on metals based on the cyanide method. This solution was removed in the second rinse tank of cadmium plating line. The concentration of cadmium in the

solution was 11.56 mg L^{-1}. The copper solution was supplied by an industrial manufacturer of printed circuit boards by sampling wastewater effluent from where the concentration of copper was 50.00 mg L^{-1}. All chemicals were obtained from Merck (Darmstadt, Germany) unless otherwise indicated.

The microalloyed aluminium composite

The microalloyed aluminium is a new material with different properties in comparison to pure aluminium. It is prepared by the microalloying of 99.8% pure aluminium with Sn, Ga, and Bi (Bojić et al. *2001*). In our studies, after the microalloying process, the material obtained was analysed by flame atomic absorption spectroscopy (FAAS), and the amounts of metals found corresponded to: 0.105% Sn, 0.098% Ga and 0.040% Bi. Through microalloying, due to the numerous defects in the crystal lattice caused by different dimensions and charges of microalloyed elements related to Al^{3+}, the oxide layer of aluminium became porous and permeable to ions (Cotton and Wilkinson *1972*, Bojić et al. *2001*). The microalloyed components generate defects in the metal structure (interstitials and vacancies in crystal lattice) and an imbalance in the charge distribution and form many microgalvanic cells. These defects decrease the energy barrier for the transport of the Al^{3+} ion from the metal to the oxide layer, and O^{2-} ion from the oxide to the metal. An after effect is an increase of ionic and electronic conductivity between 10^4 to 10^6 times, and an increase in the corrosion rate of almost the same order of magnitude. Accordingly, the stationary potential of the microalloyed aluminium is very negative, about –1.5 V/saturated calomel electrode (Rieger *1987*; Bojić et al. *2001*), and this makes the microalloy more chemically reactive than pure aluminium.

The microalloyed aluminium composite was made from an iron wire (mesh 1.2×1.2 mm, $\varnothing$ 0.6) metalized with the microalloyed aluminium via liquid metal metallization using a special gas burner (Metco, USA; Bojić et al. *2001*). The surface of the material obtained was amorphous with micro porosity in the form of fish scales, and a highly developed specific surface, making it convenient for the adsorption of different ions, molecules and colloids dissolved in water. The form of the composite in the aqueous medium is presented in Fig. 1, which shows that, besides the many local microgalvanic teams in the microalloyed aluminium, there is also a macrogalvanic cell, Fe|Al$_{\text{Micalloy}}$. Contact of the microalloyed aluminium with the iron bearer leads to the increase of anode activity and rate of dissolution (Rieger *1987*; Bojić et al. *2001*).
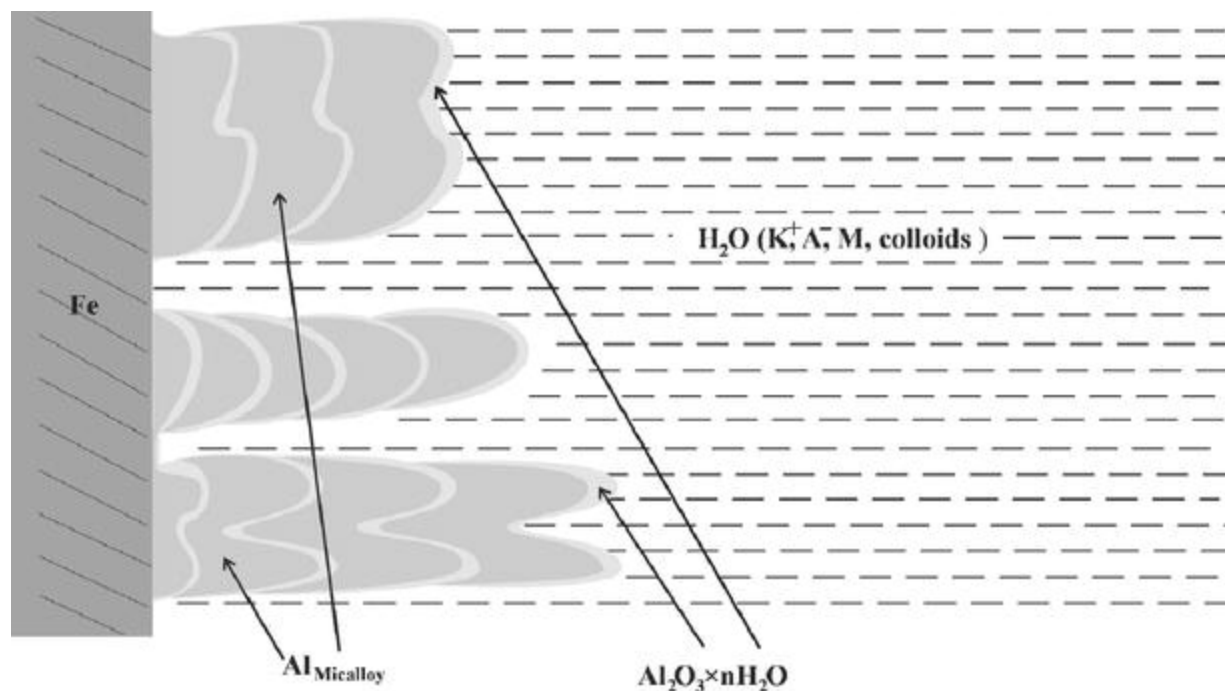
Fig. 1 A model of the structure of the microalloyed aluminium composite in an aqueous medium

The effects of the composite on pollutants in water are based on its spontaneous reaction with water (Novaković et al. *1998*a; Novaković et al. *1998*b; Bojić et al. *2001*). The main process on microanodes is the dissolution of aluminium, including the generation of Al(III) ions, via the oxidation of Al via Al^+, and Al^{2+} stages (Cotton and Wilkinson *1972*). Besides the release of OH^- ions, the main process on microcathodes is the reduction of water to H_2 via the H· stage (Cotton and Wilkinson *1972*). All of the particles, excluding the water molecules that come to the surface of the composite, may become participants in many different chemical and electrochemical processes (reduction, hydrolysis, addition). Al(III) and OH^- ions finally form an indissoluble aluminium-hydroxide that coagulates into a gelatinous, voluminous colloidal precipitate with a very developed surface, a common reagent for coprecipitation (Park et al. *2002*). For the most part, products of pollutants chemical degradation by the microalloyed aluminium composite, as well as residual undegradadet pollutant become coprecipitated by the aluminium-hydroxide during the treatment and were therefore removed from the water phase (Novaković et al. *1998*a; Novaković et al. *1998*b; Bojić et al. *2001*).

The treatment of solutions

The composite treatment time was determined according to the nature of the pollutants removed and their concentrations, which was determined to be 240 min for both cadmium and copper solutions. The experiments were done in stationary conditions in a cylindrical Plexiglas bath, with a diameter of 12 cm and a height of 15 cm. The solution in the bath was stirred by a mechanical stirrer. Two composite wires, ($10{\times}10$ cm) were bent to fit the shape of the bath, and

were immersed in the 500 -mL solution. The composite wires were fixed with glass rods so that they would dangle 3 cm from the bottom of the Plexiglas bath. The wires were immersed at the start of the composite treatment. Aliquots used for the analysis of the treated solutions were withdrawn from the bath at 30 min intervals using a pipette, transferred to flasks with glass stoppers, and left to give the $Al(OH)_3$ precipitate time to settle down. Sixty seconds before sampling, due to homogenisation of the water phase, the solution was stirred by a mechanical stirrer at 300 rpm. The aliquots were decanted, filtered and analysed by flame atomic absorption spectrometry. All experiments were performed in triplicate on the same sample.

At the end of the microalloyed aluminium composite treatment, the composite wires were removed from the solution. It was noted that at their surfaces, in the case of both metals, black amorphous powder of reduced metal was deposited during the treatment. The wires were gently washed with deionized distilled water, and the composition of their surfaces was investigated by dissolving them in diluted hydrochloric acid. After the removal of the wires, a small amount of nitric acid was added to the solution and boiled for couple of minutes to totally dissolve larger particles of reduced metal. The solution obtained was also analysed by FAAS.

Voluminous $Al(OH)_3$ precipitate, formed during the composite treatment was left to settle down separated from the water phase by decanting and then weighed. After that, the precipitate was homogenized by stirring, and a sample of 15.0 mL was taken. The sampled precipitate was weighed and dissolved by diluted HCl. The solution was filtered through black ribbon filter paper and analysed. The black powder residue that remained on the filter paper was treated with dissolved nitric acid and heated. The solution obtained was also analysed by FAAS. These analyses provided necessary information for defining the mechanism of metal removal from wastewaters.

Analytical methods

The analyses were performed by flame atomic absorption-spectroscopy, using a VARIAN SpectrAA–20 (Mulgrave, Victoria, Australia). All samples—aliquots withdrawn during the treatments, solutions obtained by the dissolving of composite wires, and solutions of $Al(OH)_3$ precipitate—were filtrated on 0.45- μm pore-sized, acid-washed nitrocellulose membrane filters (Millipore Corporation, Bedford, Mass., USA) to remove undissolved particles before analysis.

The instrumental parameters for the copper analysis were: a copper hollow cathode lamp; lamp current, 4 mA; wavelength, 324.8 nm; spectral band width, 0.5 nm; an air–acetylene flame as well as an oxidizing type of flame. The instrumental parameters for the cadmium analysis were: a cadmium hollow cathode lamp; lamp current, 4 mA; wavelength, 228.8 nm; spectral band width, 0.5 nm; an air–acetylene flame as well as an oxidizing type of flame (Standard Methods _1995_). The standard solutions for the copper determination were prepared via the dissolving of electrolyte copper (p.a. grade) in distilled HNO_3, and diluting it with deionized distilled water. The cadmium standards were prepared via the dissolving of $3CdSO_4 \cdot 8H_2O$ (p.a. grade) in deionized distilled water (Standard Methods _1995_). In regards to cadmium determination, because of low concentrations, those samples withdrawn after 180, 210, and 240 min were concentrated before analysis by vacuum evaporation to 1:10, while the rest of them were analysed directly, or after diluting.

Results and discussion

Copper and cadmium were removed from industrial wastewaters by applying a microalloyed aluminium composite in the form of metal wire without convection or stirring. The change in the cadmium and copper ions concentrations in wastewater samples during the treatments are shown in Figs. 2 and 3.
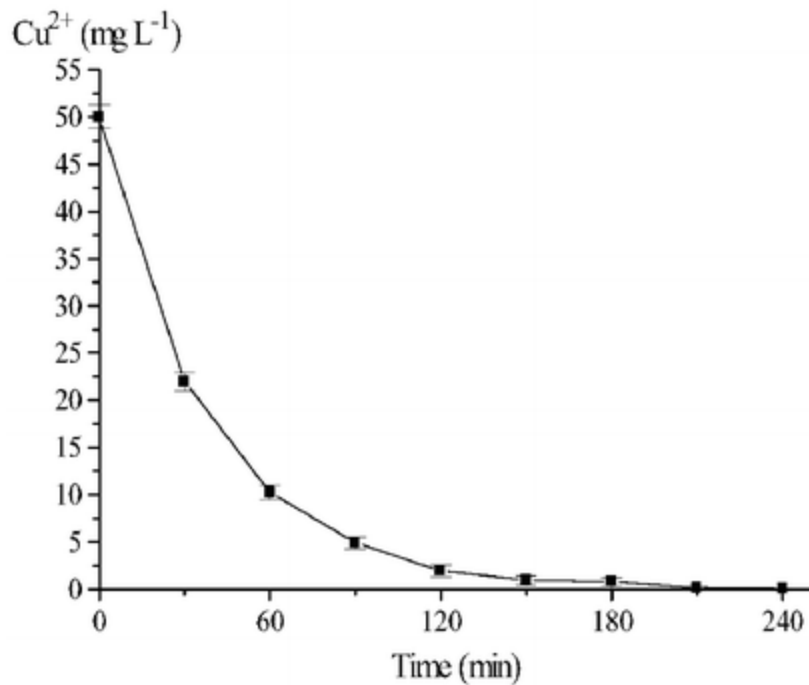

Fig. 2 Cu^{2+} concentration in wastewater during the treatment by the microalloyed aluminium composite. *Error bars* represent the standard deviation of means values of triplicate samples
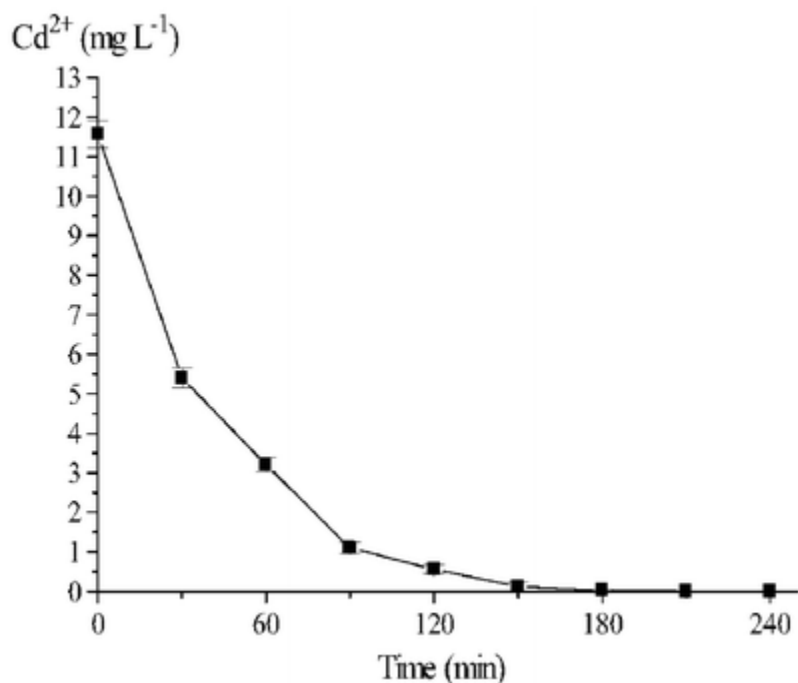
Fig. 3 Cd^{2+} concentration in wastewater during the treatment by the microalloyed aluminium composite. *Error bars* represent the standard deviation of means values of triplicate samples

In the case of both metals, the results demonstrate a strong decline of metal ions concentrations in a relatively short period of time during the composite treatment. The curves in Figs. 2 and 3 show that at the beginning of the treatment, concentrations of divalent cadmium and copper ions quickly decreased, whereby after about 120 min the total concentration change is of a magnitude of more than two orders. In the second half of the treatment, the change in the concentrations of the metal ions is significantly minor.

The total decrease of copper concentration is approximately 1,300-fold. The final concentration is 0.02 mg L^{-1}, which is below the maximal allowed concentration for drinking water or 0.05 mg L^{-1} (Standard Methods *1995*). Analyse of the composite wires surface show that at the end of the treatment, there was 1.8 mg of metal copper in the form of a black amorphous powder. After dissolving the $Al(OH)_3$ precipitate in hydrochloric acid, 3.9 mg of copper in form of indissoluble $Cu(OH)_2$ was found in the solution. The amount of deposit on the filter paper left after the filtering of the precipitate solution dissolved in HNO_3, was 18.7 mg of metal copper.

The final concentration of cadmium at the end of the treatment was 0.004 mg L^{-1}, which was also below the maximal allowed concentration of 0.005 mg L^{-1} (Standard Methods *1995*). The treatment time could be even shorter in a flow system. In this way, the diffusion of the metal species (both Cu^{2+} and Cd^{2+}), which is enlarged, enables the rate of process to be increased three or even four times. This flow system in full scale shows good preliminary performances.

At the end of the treatment, there was 0.52 mg of metal cadmium on the composite wires taken

from the cadmium plating rinse water sample. Analysis showed that the $Al(OH)_3$ precipitate contained 2.1 mg of cadmium in the form of $Cd(OH)_2$, and 2.8 mg of metal cadmium. The amount of Cd(II) in $Al(OH)_3$ is very low, and it is significant for further handling with the precipitate, providing cadmium toxicity. In the following, the mechanism of copper and cadmium removal from water are discussed in detail.

Besides the high decrease in the concentrations of both pollutants, the results of this study also show the differences in the mechanisms for removal of cadmium and copper. These differences are in accordance with the metals nature, namely its electropotential. The results of $Al(OH)_3$ precipitate analyse show that copper is removed in a greater amount from wastewater in a metal form than as copper-hydroxide, and the ratio of $[Cu]/[Cu(OH)_2]$ is above five. Because of the positive electropotential of copper, the main process during the composite treatment is the reduction of Cu^{2+} ions in contact with the surface of the composite wires. The coprecipitation of Cu^{2+} ions by aluminium-hydroxide is of minor significance. In the case of cadmium, the ratio of reduced metal and $Cd(OH)_2$ found in $Al(OH)_3$ at the end of the treatment is only about 1.5. This indicates that probability of the reduction of Cd^{2+} ions during the composite treatment is less than that for Cu^{2+}, because of its negative electropotential.

Conclusion

Microalloyed aluminium composite is a powerful device for the removal of cadmium and copper from wastewaters. Metal concentration change rates are the highest at the beginning of the treatment, and in time, they show a tendency to decrease. After 100–120 min, concentrations of both metals are low enough to let treated water collect, and after 200–240 min, they were even below the maximal allowed concentrations for drinking water. The fact that the main part of cadmium and copper is removed from water in a metal form, and that the minor part is removed in the form of hydroxides, indicates that the mechanism for metals to be removed from the water phase is mainly based on reduction, and to lesser extent on coprecipitation. If the kinetic aspect of treatment is to be considered, an even shorter time of treatment could be set in flow conditions.

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