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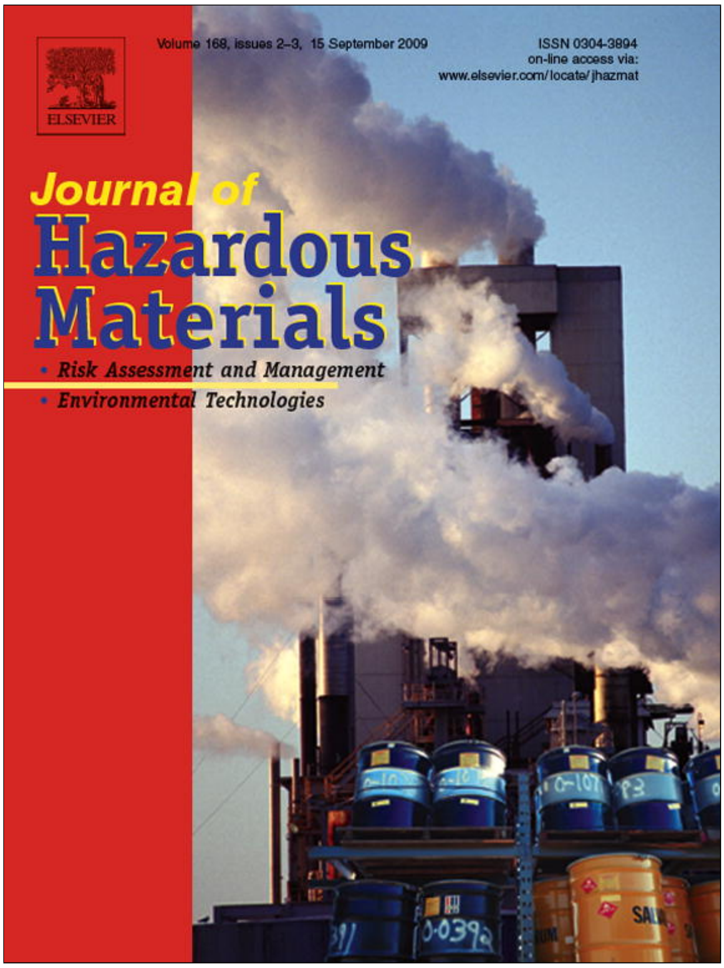

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Removal of Cu^{2+} and Zn^{2+} from model wastewaters by spontaneous reduction–coagulation process in flow conditions

Aleksandar Lj. Bojic*, Danijela Bojic, Tatjana Andjelkovic

Department of Chemistry, Faculty of Sciences and Mathematics, University of Nis, Visegradska 33, 18 000 Nis, Serbia

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ABSTRACT

The treatment of model wastewaters containing heavy metals by spontaneous reduction–coagulation process using micro-alloyed aluminium composite (MAlC) in a laboratory semi-flow system (SFS) has been investigated. Several working parameters, such as treatment time, pH, initial metal concentration and flow rate were studied in an attempt to achieve a higher removal capacity. The residual concentrations of metals were at admissible levels after only 20 min of treatment. Removal rate of Zn^{2+} was greater at neutral pH than at acid or basic, while Cu^{2+} removal was less affected by pH. Removal constants of both metals decreased as initial metal concentration increased from 20 to 200 mg L^{-1}. In mixed wastewaters the presence of copper caused increase of Zn^{2+} removal efficacy, however, the copper removal was not affected by zinc. The removal mechanisms depend on metals nature and pH: copper was mainly removed by reduction, while zinc by precipitation as hydroxide. The kinetic of process was mass-transport limited, thus increasing of flow rate accelerated removal of metals. The method was found to be highly efficient and faster compared to conventional treatments.

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1. Introduction

The effluents generated by different industries, including metal finishing, electroplating, printed circuit, non-ferrous metal works, motor vehicles, usually contain heavy metal ions in concentrations much higher than the permissible levels [8,15,16]. Due to their high toxicity for humans, animals and plants, wastewaters containing heavy metals are strictly regulated and must be treated before being discharged in the environment [6,2]. When addressing surface and groundwater pollution problems, heavy metals including cadmium, copper, chromium, lead and zinc should be ranked in priority based on their toxicity and persistent characteristics. In industrial wastewater streams and urban runoff samples, copper and zinc are detected over 90% frequency, while cadmium, lead and chromium to a lesser extent [8,9]. Copper is not considered very harmful to human health, but at high concentrations in drinking water, it may cause an unpleasant taste and affect certain individuals suffering from a copper metabolism disorder called Wilson disease [4]. Its ingestion beyond the permissible level [13] causes various types of acute and chronic disorder in man, such as hemochromatosis, gastrointestinal catarrh, cramps in the calves and a skin dermatitis brasschills, usually accompanied by high fever [4]. Industrial wastewaters usually contain copper in a concentration range from about 5 to 250 mg L^{-1} [8]. Zinc is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of zinc, too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia. Very high levels of zinc can damage the pancreas, disturb the protein metabolism, and cause arteriosclerosis [4]. It may be found in wastewaters in concentration range from 10 to 400 mg L^{-1} [8].

Concentrations of these metals higher than 100 mg L^{-1} can be easily decreased by means of an electrochemical treatment [3,6], reverse osmosis [11,14], zerovalent iron [7,12] or chemical treatment of the wastewater [2,8]. However, the application of methods mentioned above becomes costly at lower metal concentrations. Therefore, the usage of micro-alloyed aluminium composite (MAlC) represents an attractive means for heavy metals removal from wastewater by spontaneous reduction–coagulation process, in terms of both removal ability and cost effectiveness.

The composite consists of micro-alloyed aluminium (MAl) coated over a thin iron net. Its mechanism of action is based on the several physico-chemical processes and the *in situ* formation of the coagulant, due to its spontaneous reaction with water [1,10]. The major processes are adsorption, reduction, hydrogenation, hydrolysis and coagulation, operating synergistically to degrade and remove variety of pollutants from water, similarly as in process of electrocoagulation [17,18]. An examination of processes occurring in the MAlC treatments shows that the main reaction at the

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* Corresponding author. Tel.: +381 63 106 40 16; fax: +381 18 533 014.
E-mail address: bojic@bankerinter.net (A.Lj. Bojic).

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micro-anodes is dissolution of aluminium:

$$\mathrm{Al} \rightleftarrows \mathrm{Al}^{3+} + 3e \qquad (1)$$

and on micro-cathodes reduction of water to H_2, with forming of OH^- ions:

$$2\mathrm{H_2O} + 2e \rightleftarrows \mathrm{H_2} + 2\mathrm{OH}^- \qquad (2)$$

Every particle in water treated by the composite may become a participant in mentioned physico-chemical processes. At the micro-cathodes may occur direct reduction of metal cations [1,10,18]:

$$\mathrm{Me}^{n+} + ne \rightleftarrows \mathrm{Me}^0 \qquad (3)$$

or hydrogenation of unsaturated organic compounds:

$$\mathrm{R{-}CH{=}CH_2} + 2\mathrm{H}^\bullet \rightleftarrows \mathrm{R{-}CH_2CH_3} \qquad (4)$$

in bulk water phase occurs hydrolysis and precipitation of metal ions [1,10,18]:

$$\mathrm{Me}^{n+} + n\mathrm{OH}^- \rightleftarrows \mathrm{Me(OH)}_n \qquad (5)$$

and hydrolysis of halogenated organic compounds:

$$\mathrm{R{-}Cl} + \mathrm{OH}^- \rightleftarrows \mathrm{R{-}OH} + \mathrm{Cl}^- \qquad (6)$$

In addition, Al^{3+} and OH^- ions generated at the micro-electrodes, react in the bulk wastewater to form insoluble $Al(OH)_3$:

$$\mathrm{Al}^{3+} + 3\mathrm{OH}^- \rightleftarrows \mathrm{Al(OH)_3} \qquad (7)$$

The aluminium hydroxide flocks act as adsorbents and/or traps for ions, molecules or suspended particles thus removing them from the solution by sorption, co-precipitation or electrostatic attraction followed by coagulation [1,10,18].

The MAlC has been successfully used to treat solutions of trihalomethanes, with removal efficiencies as high as 99%. A similar success was obtained with treatment of textile dyes, natural organic mater and pesticides containing waters. In addition, studies of Bojic et al. [1] and Purenovic et al. [10] proved that the MAlC is an effective means for the treatment of heavy metals containing solutions. In the present work, the efficiency of the MAlC in removing copper and zinc from model wastewaters was reported. The effects of treatment time, pH, initial metal concentration and flow rate, on the removal efficiency are explored and discussed in order to define the optimum operational conditions.

2. Materials and methods

2.1. Reagents

All chemicals used were of reagent grade and used without further purification. Deionized water (<5 μS cm^{-1}) was used to prepare all aqueous solutions. $CuSO_4{\cdot}5H_2O$, $ZnSO_4$ and HNO_3 were purchased from Merck, Germany. NaOH, $NaNO_3$ and H_2SO_4 were supplied from Zorka (Serbia).

Stock model wastewater solutions of 1000 mg L^{-1} copper or zinc were prepared by dissolving the required amounts of copper sulphate or zinc sulphate in deionized water. Solutions of lower concentrations were prepared by proper dilution. Model wastewaters contained 50 mg L^{-1} of Cu^{2+} or Zn^{2+}, or Cu^{2+} and Zn^{2+} in mixture in the same concentration. The pH of the solutions was adjusted pH-metrically to the required value with sulphuric acid or sodium hydroxide (10^{-2} M), without buffering. Conductivity of the model wastewater was adjusted to 20 mS cm^{-1} by addition of sodium nitrate in order to reduce the IR-drop [17].

The micro-alloyed aluminium composite was made of an iron net coated with the MAl (Al with micro-amounts of Sn, Ga and Bi), by metal spraying. The obtained composite material had a shapeless surface with many micro-pores and large specific surface area, with very negative open circuit potential. Detailed physico-chemical characteristics of the micro-alloyed aluminium composite have been presented previously [1,10].

2.2. Experimental procedure

Batch experiments were carried out using the semi-flow system [1]. Equipment, shown schematically in Fig. 1 comprised several parts, preferably made of high-density polyethylene. A composite chamber of 1.0 L volume, with the MAlC wires placed perpendicular to the direction of the water flow. A main bath of 10 L volume for storing the water solution. Vertical barriers were added at the bottom of the main bath to disable movement of $Al(OH)_3$ precipitate formed during the treatment. A peristaltic pump and a thermostat connected to water jackets of the main bath and the composite chamber. The composite chamber was located above the main bath and a peristaltic pump transported aqueous solutions to it. After passing through the composite chamber, where pollutants were exposed to the MAlC, the solution was returned to the main bath by free fall. This formed a closed loop to enable the system to operate in a flow mode. Entering and returning tubes of the composite chamber were placed in the main bath, in order to prevent plugging of $Al(OH)_3$ precipitate, accumulated on the bottom.

Before treatments, composite wires were pre-treated by diluted H_2SO_4 (pH 1–1.5) and then were rinsed several times with deionized water to remove the oxide and/or passivation layer from surfaces. Every experiment was started with 8.0 L of metal solution. Solutions were equilibrated at 25 °C, transferred to the main bath and peristaltic pump was run. During the MAlC treatment, the temperature was kept at 25 ± 0.5 °C. To follow the progress of the treatment, 10 cm^3 samples were periodically withdrawn from the surface layer of water phase in the main bath where there was laminar flow and minimal amount of $Al(OH)_3$. Samples were left to stand to settle down and filtered using a 0.45 μm pore size acid-washed cellulose nitrate membrane filter (Millipore Corporation, Bedford, MA, USA) and acidified with H_2SO_4 directly after sampling. The residual concentrations of metal ions were determined by flame atomic absorption spectrophotometer Varian Spectra A-20 (Mulgrave, Victoria, Australia). During the treatments, pH was monitored by digital pH meter (HACH SensIon 3, USA), with a HACH gel-filled combination glass electrode and the conductivity was measured with a conductivity meter (HACH SensIon 5). At the end of the treatment, the solution was decanted and the total $Al(OH)_3$ precipitate was dried and weighed. In the case of zinc treatment,

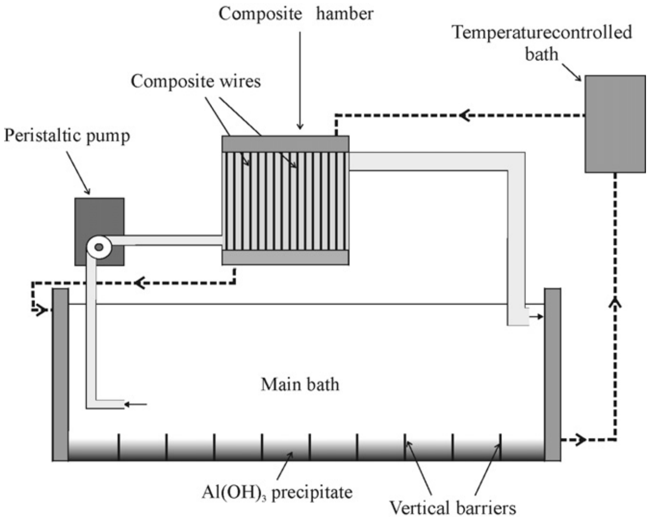

Fig. 1. Schematic diagram of the semi-flow system.

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representative sample of precipitate was weighed and treated by slightly alkaline NaCN solution, to extract zinc that was precipitated as hydroxide and co-precipitated with $Al(OH)_3$. Obtained solution was acidified with H_2SO_4 and boiled to remove CN^- as HCN, in order to destroy cyanide complex and determine zinc using FAAS. The rest of precipitate, containing zinc as zerovalent metal, was dissolved with H_2SO_4. Obtained solution was analysed by graphite furnace (GF) AAS, rather than flame analysis due to interferences of dissolved solids high concentration. For speciation of copper forms, representative sample of precipitate was dissolved with NaOH. Copper removed from model wastewater solution in the form of $Cu(OH)_2$ and in co-precipitated form was also dissolved in that way. Solution was filtered and analysed using GFAAS. Undissolved residue was zerovalent copper removed by reduction. It was dissolved by diluted H_2SO_4 with small amount of concentrated HNO_3 and analysed using FAAS.

After the treatment, the composite nets were gently washed by deionized distilled water. Surface layer, with deposited zerovalent metal, was dissolved in a diluted H_2SO_4. In the case of copper treatment, small amount of concentrated HNO_3 was added and boiled for a couple of minutes to dissolve larger particles of deposited metal. The obtained solution was analysed with FAAS. The total amount of metal removed by hydroxide precipitation and co-precipitation was calculated over to the whole $Al(OH)_3$ precipitate. The total amount of metal removed by reduction was the sum of zerovalent metal found in whole $Al(OH)_3$ precipitate and metal deposited on the composite nets. All experiments were carried out for 65 min continually. Triple replicates of each experiment were carried out in order to ascertain the degree of variation in the experimental procedure. Control experiments were done under identical conditions, except that no composite wires were present in the composite chamber in order to determine the degree of metal ion uptake by the polyethylene. The adsorption of metals was found to be negligible.

Dissolution rate of the MAlC was determined using the modified SFS, where rectangular main bath was replaced by cylindrical vessel, placed on magnetic stirrer to enable homogenization of $Al(OH)_3$ suspensions. During the treatment, solutions were strongly stirred, and the samples were taken from the bottom of the bulk solution near main bath, where was the greater turbulence. The rest of conditions in experiments were the same as previous.

3. Results and discussion

3.1. Effect of treatment time

Experiments were done with synthetic wastewaters containing one single metal at initial concentration 50 mg L^{-1}. Fig. 2 shows the residual concentrations of Cu^{2+} and Zn^{2+} ions against treatment time. Initial pH was 6.0 and flow rate was 90 L h^{-1}. The concentrations of copper and zinc decreased almost linearly by time. Initial concentrations of each metal were removed below maximum contaminant level (MCL) for drinking water [13] after only 30 and 40 min, respectively. However, after less than 20 min concentrations of metals were reduced to admissible levels for discharging of wastewater to recipients.

3.2. Effect of initial pH

It has been established in previous studies that pH has a considerable effect on the efficiency of the MAlC treatments, referring to both processes: reduction and coagulation [1]. In this study, the pH was varied in the range from 2 to 12 in an attempt to investigate the influence of this parameter on the removal of Cu^{2+} and Zn^{2+} ions from model wastewaters containing 50 mg L^{-1} of one single metal. Removal efficiencies of copper and zinc as a function of the initial pH are presented in Fig. 3.

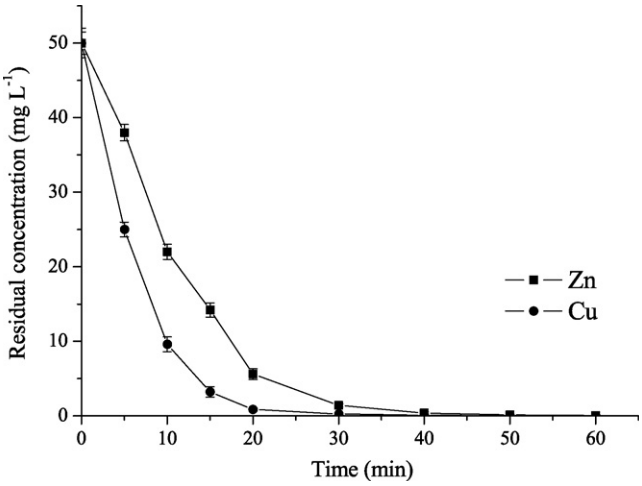

Fig. 2. Residual concentrations of Cu^{2+} and Zn^{2+} ions during the MAlC treatment of model wastewaters containing one single metal. The experiments were done in the SFS. Initial concentration of the metals was 50 mg L^{-1}, initial pH was 6.0, temperature was kept at 25 ± 0.5 °C and flow rate was 90 L h^{-1}.

The removal efficiency of copper after 15 min of MAlC treatment was very high and reached values from 90 to 98.5%, against initial pH (Fig. 3). Results also show that removal yield is the lowest at neutral pH range. After 15 min of treatment, the highest removal efficiency of copper has been obtained in solution with initial pH 12.

Analysis of the composite nets surface and $Al(OH)_3$ precipitate after the treatments, show that the removal pathways of copper involve the direct reduction on the micro-cathodes, in the form of zerovalent metal and the precipitation as hydroxide with partial co-precipitation on $Al(OH)_3$ [10]. Similar mechanism is presented in the study of Heidmann and Calmano [18], which corresponds with aluminium electrocoagulation removal of heavy metals. Although the electrocoagulation is not spontaneous process as the suggested process is. At acid initial pH, from 2 to 4, copper was dominantly removed in the reduced form. It was noted that at the very beginning of the treatment, black amorphous powder of reduced metal start deposited on the nets' surface [10]. This happen continually during all treatment. In these conditions, a low amount of Cu^{2+} ions was removed by hydroxide precipitation and co-precipitation, because of increasing of pH during the treatment and arising conditions for hydroxide formation. Results show that in the sample with initial pH 2 only 2.5% of total removed copper was removed as $Cu(OH)_2$, because more than 95% was already removed as zerovalent metal in the first 15 min, when pH was less than 4 (Fig. 3). To the end of the treatment, pH gradually increased (Fig. 4) and residual copper was mainly removed as hydroxide. In accordance with this, in wastewater solution with initial pH 4 almost 90% of copper was removed as zerovalent metal and the rest was precipitated as hydroxide.

Fig. 5 shows that amount of copper removed by precipitation as $Cu(OH)_2$, increased with initial pH to neutral environment. When the initial pH was kept in the range from 6 to 8, amounts of copper removed as zerovalent metal and as $Cu(OH)_2$ were nearly equal. These conditions equalize the rates of concurrent processes: reduction and hydroxide precipitation. Reduction activity of the MAlC were the least at neutral pH (Fig. 6) and at the other side solubility of $Cu(OH)_2$ and $Al(OH)_3$ was lower in that pH range (isoelectric points are 6.6 and 6.2, respectively) [5]. However, with further increase of initial pH to basic medium, amount of copper removed as zerovalent metal resume its growth. At pH 10 about 60% of

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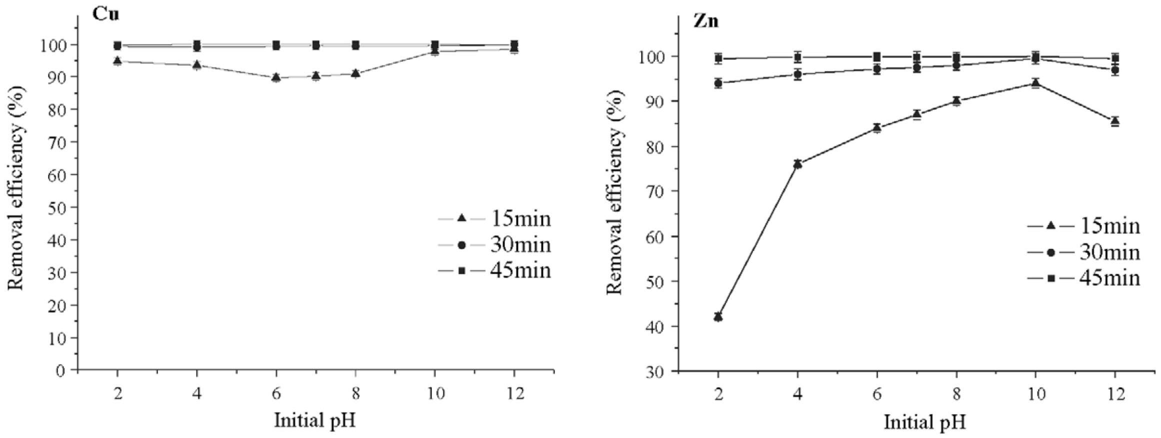

Fig. 3. Effect of initial pH on Cu^{2+} and Zn^{2+} ions removal from model wastewaters containing one single metal. Experiments were done in the SFS. Initial concentration of metal was 50 mg L^{-1}, temperature was kept at 25 ± 0.5 °C and flow rate was 90 L h^{-1}.

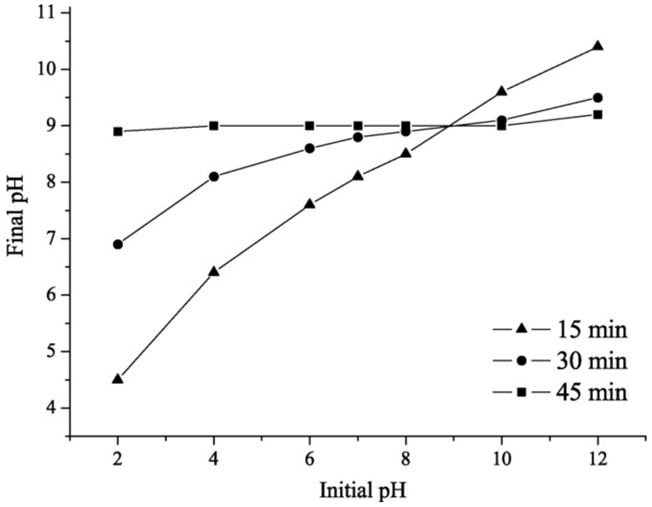

Fig. 4. Variation of pH during MAlC treatment as a function of initial pH.

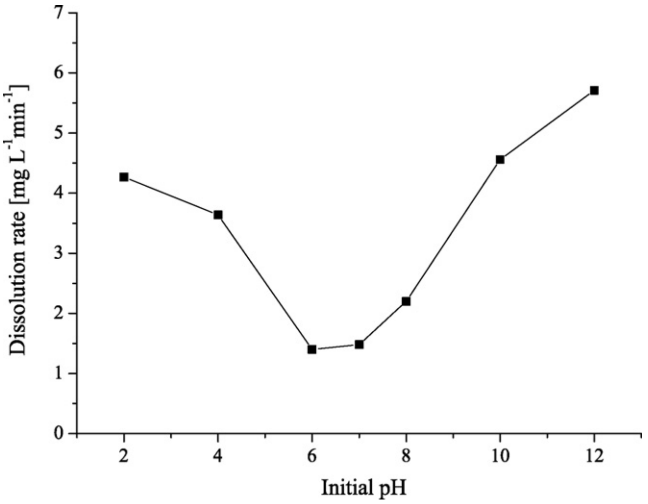

Fig. 6. Dissolution rate of the MAlC as a function of initial pH.

copper was removed as zerovalent metal and at pH 12 it increases to 75% (Fig. 5).

These results suggest that the initial pH have greater influence on the form of removed copper than to removal efficiency, which is in accordance with its chemical nature (electropositive metal, $E^\circ = +0.34$ V) and reduction of Cu^{2+} ions by MAlC is thermodynamically favored. Removal mechanism and efficiency were also attributed to composite behavior in function of initial pH. Fig. 6 shows that dissolution rate of the MAlC, as amphoteric metal, increase at pH less than 6 and higher than 8, which leads to appearance of soluble Al^{3+} in the samples with low initial pH and to monomeric $Al(OH)_4^-$ when the initial pH is high. Its reduction activity follows the same trend: at initial pH 7 dissolution rate of the MAlC was 1.4 mg L^{-1} min^{-1}, while at pH 2 and 12 it was

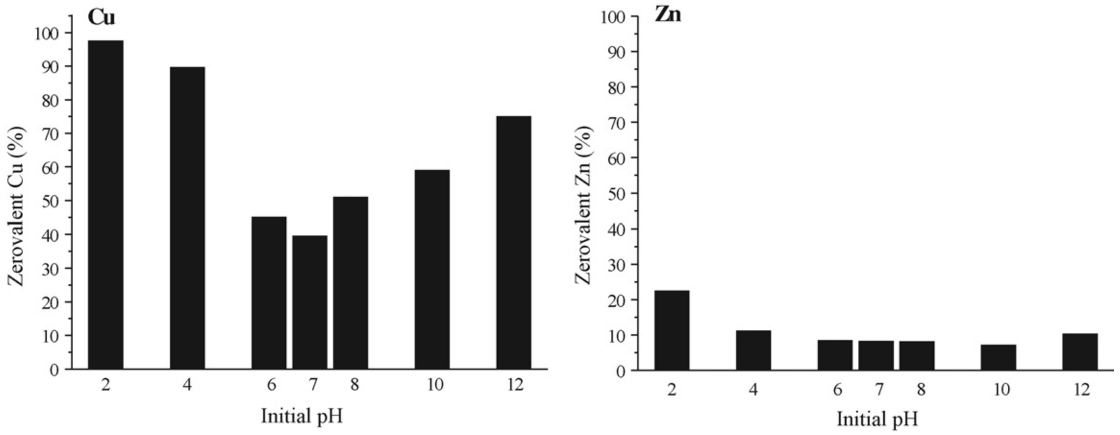

Fig. 5. Amount of copper and zinc removed as zerovalent metals in function of initial pH after 60 min of the MAlC treatment.

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4.27 and 5.71 mg L^{-1} min^{-1}, respectively. Curve of effect of initial pH on copper removal after 15 min of the MAlC treatment (Fig. 3) is very similar to curve of the composite dissolution rate (Fig. 6). Thus, removal efficiency of copper was the lowest in neutral environment. Low amount of copper removed as $Cu(OH)_2$, in solution with initial pH 2 (Fig. 3), appears because of pH increasing during the treatment and arising conditions for hydroxide formation. Although the pH of the bulk solution is too low for hydroxide formation, copper can precipitate in zones around micro-cathodes because of local alkalization [18]. Results in Fig. 4 show that after 40–45 min of treatment, pH of all model wastewaters became about 9. In the experiments without metal addition, the pH change is the same. This is in accordance with our previously published work [1], which show buffering effect of the MAlC|H_2O system. Very high efficiency of Cu^{2+} removal from alkaline wastewaters, greater than from acid one, is result of suitable conditions not only for reduction and also for precipitation as $Cu(OH)_2$ and co-precipitation on $Al(OH)_3$ (Fig. 3).

Results in Fig. 5 also show, that after 30 min of the treatment, residual concentrations of Cu^{2+} ions in all wastewaters were very low (below MCL) and treatment seemed to be less affected by the initial pH. After 45 min in all samples, the concentrations of Cu^{2+} ions became undetectable, whereby influence of the initial pH disappear, because of buffering effect of the MAlC|H_2O system. This result is quite meaningful for copper removal by the MAlC, since the pH of different industrial wastewaters polluted with this metal varies in very high range, which allows it to be directly treated without further pH adjustment.

Contrary, influence of the initial pH to removal of zinc is more significant and quite different. At the initial pH 2 removal yield of Zn^{2+} after 15 min was very low and only about 42% of the metal was removed (Fig. 3). With increase of the initial pH, a dramatic increase of removal efficiency was observed. The highest removal rate was noted at initial pH 10. With further increasing of the initial pH to 12, removal efficiency of Zn^{2+} decreased. Analysis of the composite surface and $Al(OH)_3$ precipitate show that zinc was mainly removed by precipitation as $Zn(OH)_2$ and by co-precipitation on $Al(OH)_3$ coagulant, and much less by reduction. Rate of zinc removal forms (Zn^{2+}/Zn^0), depends of the initial pH (Fig. 5), but less related to copper.

High composite activity in acid environment, has low significance for removal of zinc, because Zn^{2+} could not be reduced in this conditions according to its negative redox potential ($E^\circ = -0.76$ V). In addition, one supposed that significant part of eventually reduced Zn^{2+} ions were immediately dissolved at low pH. Because of that in model wastewaters with acid pH, removal of zinc start after specific period required for exceeding pH needed for hydroxide formation. Likewise copper, it is also possible that zinc can precipitate within the local zones of high pH around micro-cathodes, even pH of the bulk solution is too low for the overall precipitation of $Zn(OH)_2$ [18]. However, Fig. 5 shows that only in wastewater with the initial pH 2 significant amount of zinc was removed in reduced form (about 22%), while in samples with neutral initial pH amount of zerovalent metal was about 7–8%. Fig. 3 shows that increase of the initial pH led to more effective removal, because of increasing of OH^- ion concentration necessary for $Zn(OH)_2$ and $Al(OH)_3$ formation. The removal yield of zinc reached a maximum in wastewater solution with initial pH 10, due to high composite activity and relatively low solubility of both hydroxides in these conditions. High efficiency of zinc removal in sample with initial pH 10 might be also ascribed to fast achieving of final pH 9 (Fig. 4), which additionally improves hydroxide formation. In contrast, in wastewater with initial pH 12, besides significant increase of the MAlC activity, a dramatic decrease of the removal efficiency of zinc was observed, because zinc and aluminium hydroxides had been transformed to soluble ${ZnO_2}^{2-}$ and ${Al(OH)_4}^-$ species [5]. At pH 12, removal of Zn^{2+} from wastewater started at pH value appropriate for hydroxide precipitation. In addition, at this pH amount of zinc removed as zerovalent metal was much greater than at neutral initial pH (Fig. 5).

After a 30 min of treatment effect of initial pH at zinc removal yield dramatically decreases (Fig. 3). Removal efficiency continually increased with increasing of the initial pH from 2 to 10, but with quite less rate according to the first 15 min of treatment. In addition, after that period decrease of efficiency with pH change from 10 to 12 was less than after 15 min. After 45 min of treatment, influence of the initial pH was negligible, because pH in all model wastewaters became equal—about 9 (Fig. 4). Final concentrations of Zn^{2+} were in all solutions below MCL, which is of great importance for application of the MAlC for purification of various wastewaters in wide initial pH range.

3.3. Effect of initial metal concentration

The effect of initial metal concentration on the removal rate was examined with several solutions containing concentrations from 20 to 200 mg L^{-1} of single metals.

Fig. 7 shows the change of the residual concentrations of Zn^{2+} with the initial concentration. As expected, it appears that the removal rate was decreased upon increasing initial concentration. However, decreasing trend was not linear with increase of the initial metal ion concentration, which is presented in Fig. 8.

At lower initial concentrations of zinc, in the range from 20 to 100 mg L^{-1}, there was low and almost linear drop of rate constant ($tg\alpha = 1.37 \times 10^{-4}$, $R^2 = 0.99$). However, with further increase of the initial concentration to 200 mg L^{-1}, decrease of removal rate was greater than expected ($tg\alpha = 2.35 \times 10^{-4}$, $R^2 = 0.921$). Decrease of zinc removal rate with increasing of metal concentration could be principally attributed to the saturation of composite surface by metal ions. This appears to be due to the increase in the number of ions competing for the available micro-cathodes on the surface. In addition, typical mass-transport controlled kinetics of pollutants removal by the MAlC is another factor which limitate removal rate of zinc and at higher concentrations, more metal ions are left in solution [1].

Fig. 8 shows that the removal rate of Cu^{2+} slightly decreased with increasing initial concentration. As a difference of zinc, here k_{obs} decline almost linearly in the whole investigated range from 20 to 200 mg L^{-1}. Slope of the curve k_{obs} vs. metal concentration was 8.76×10^{-5} ($R^2 = 0.981$), much less than for zinc.

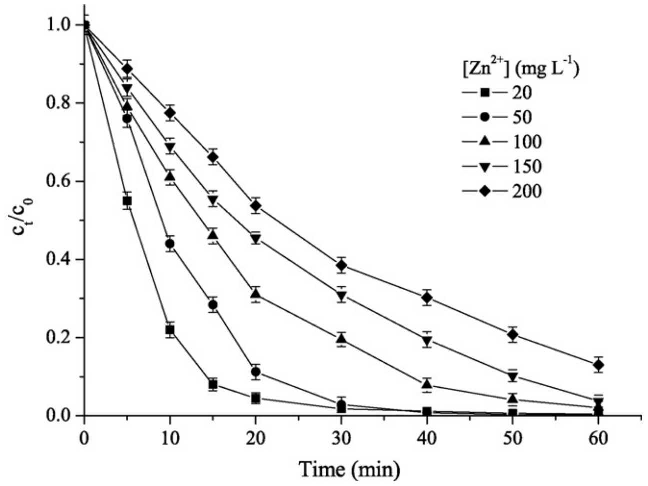

Fig. 7. Effect of initial concentration on the removal efficiency of Zn^{2+} from model wastewater. Experiments were done in the SFS, initial pH was 7.0, temperature was kept at 25 ± 0.5 °C and flow rate was 90 L h^{-1}.

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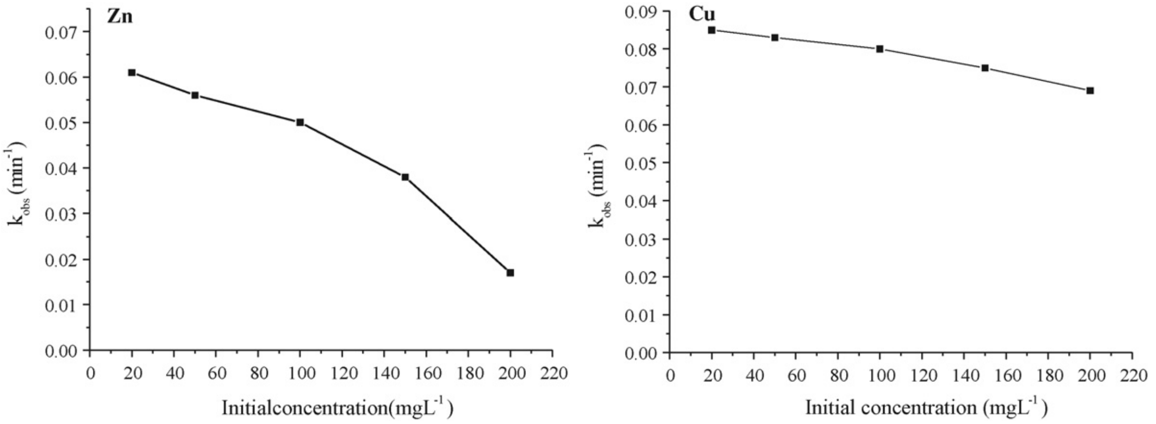

Fig. 8. Rate constants of Cu^{2+} and Zn^{2+} ions removal in function of the initial metal concentration.

Generally, it is found that the copper accelerates the MAlC corrosion and enhance its dissolution rate. As electropositive metal, after reduction and deposition on composite surface, copper formed microgalvanic cell in which represent cathode and MAl anode. By that, open circuit potential was lowered and the MAlC became a stronger reducing agent. This effect competes with negative effects of increasing of initial metal concentration and saturation of composite surface and because of that trend of decrease of removal efficacy with initial concentration is lower related to zinc.

Investigation of metal ions interaction shows that in presence of copper, removal efficacy of zinc apparently increases (Fig. 9). Result show that zinc removal rate significantly increases with copper concentration. Enhancement of zinc removal efficiency in the presence of copper is the result of composite activation by electropositive metal. Deposited zerovalent copper enlarges reduction potential of the composite, as in the mentioned treatment of copper single metal solution. Also, it can be assumed that Zn^{2+} ions could be easier reduced at new micro-cathodes that arised by deposition of zerovalent copper on the composite surface, providing a better medium for transfer of electrons released by aluminium dissolution (Eq. (1)). Slope of the curve k_{obs} vs. initial Cu^{2+} concentration decreases at higher concentrations, probably because of saturation of composite surface by metal ions, as a result of high initial concentration (Fig. 8). On the contrary, presence of zinc showed no influence on the removal rate of Cu^{2+} ions (result not shown).

3.4. *Effect of flow rate*

In the previous work, it was found that in stationary conditions (batch system) efficiency of water treatment by the MAlC was rather low [10]. Application of the semi-flow system in later studies shows better results because of convective transport [1]. This study evaluated effect of convection on the copper and zinc removal, by varying flow rate from 1 to 120 $L\,min^{-1}$. Fig. 10 shows that the removal efficiency of Cu^{2+} and Zn^{2+} ions significantly increased with the flow rate. Observed rate constants of copper removal in function of flow rate, increased by a factor of about three, in the investigated range.

The greatest change of k_{obs} in copper removal was noticed during the increase of flow rate from 1 to 20 $L\,h^{-1}$ ($tg\alpha = 7.15 \times 10^{-4}$, $R^2 = 0.91$). This jump suggests that convection play extremely significant role in removal of copper, considering that at the lowest flow rate (1 $L\,h^{-1}$), system practically works in stationary conditions (batch system). With further increase of the flow rate from 20 to 120 $L\,h^{-1}$ removal rate of copper increased almost linearly ($R^2 = 0.998$). In the case of zinc, increase of k_{obs} with flow rate are rather less. The slopes of the curve k_{obs} vs. flow rate for copper was 4.89×10^{-4} and for zinc 3.051×10^{-4} (Fig. 10). Also, it can be seen that, besides generally less effect of the flow rate for removal of zinc, there is absence of k_{obs} jump at the beginning of curve (1–20 $L\,h^{-1}$), which leads to its linearity in the whole range of flow rate ($R^2 = 0.989$).

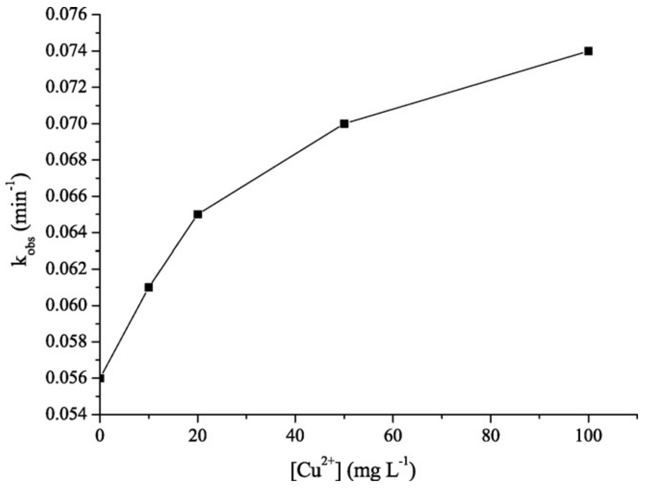

Fig. 9. Effect of Cu^{2+} ion on the removal efficiency of zinc. Experiments were done in the SFS, initial pH was 7.0, temperature was kept at 25 ± 0.5 °C and flow rate was 90 $L\,h^{-1}$.

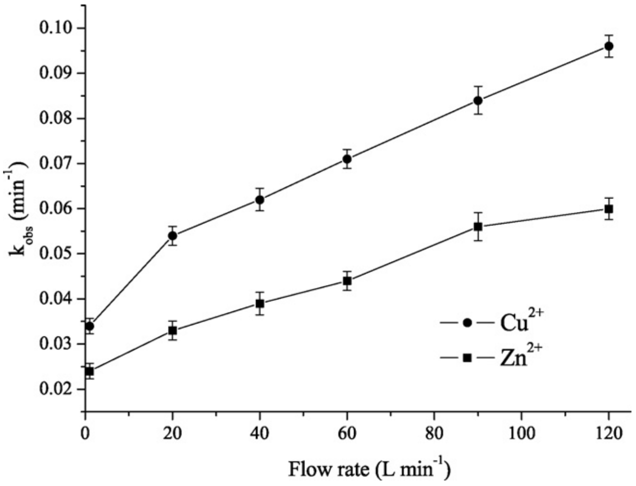

Fig. 10. Effect of flow rate on the removal efficiency of Cu^{2+} and Zn^{2+} ions from model wastewaters containing one single metal. Experiments were done in the SFS, at flow rates: 1, 20, 40, 60, 90 and 120 $L\,h^{-1}$, initial concentration of metal was 50 $mg\,L^{-1}$, initial pH was 6.0 and temperature was kept at 25 ± 0.5 °C.

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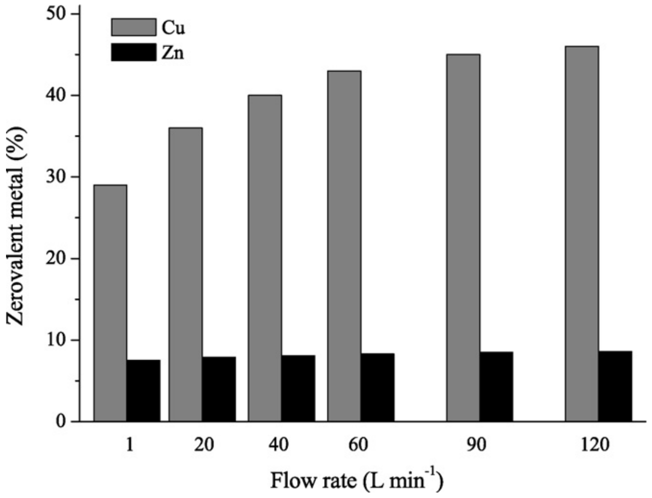

Fig. 11. Amounts of Cu^{2+} and Zn^{2+} ions removed from model wastewaters as zerovalent metals in function of flow rate, after 60 min of the MAlC treatment.

In a heterogeneous system, MAlC|H_2O, main reactions occur at the composite surface. The characteristic of those systems is mass-transport control of process and the MAlC efficiency is strongly affected by convection. However, it is not recommended to increase the flow rate to more than 120 L h^{-1} due to turbulent flow through the main bath resulted by $Al(OH)_3$ precipitate starts moving from the bottom of the main bath and migrating with fluid stream through the SFS [1]. In addition, $Al(OH)_3$ in contact with composite nets in the composite chamber may fill meshes and reduce available surface of composite nets.

Convection increases probability of metal ions contacts with composite surface, which accelerate the removal rate. Results show that this phenomenon is more significant for copper than zinc, because its mechanism of removal is based on reduction to zerovalent metal (Fig. 11).

Fig. 11 shows that the amount of copper removed as zerovalent metal increased by a factor of about 1.6, when the flow rate was increased from 1 to 120 L min^{-1}. In the same conditions, the change of zinc removed as zerovalent metal in the function of flow rate is negligible (Fig. 11). The effect of the flow rate at zinc removal is less, because its removal mechanism is mainly based on precipitation as $Zn(OH)_2$ and co-precipitation on $Al(OH)_3$ dominantly formed in bulk water phase, away of surface.

4. Conclusions

The results of this study have shown the applicability of the micro-alloyed aluminium composite in the treatment of wastewater from metal finishing industry containing copper and zinc in wide range of the initial pH. Using the MAlC treatment heavy metals are removed from water by direct reduction at the micro-cathodes on the composite surface, as hydroxides by the hydroxyl ions formed in process of water electrolysis and by co-precipitation with aluminium hydroxides. Removal efficiency is high and after less than 40 min, residual concentrations of both metals are below MCL for dinking water. The slower removal of zinc compared to copper is attributed to the removal mechanisms. Copper, as a noble metal, was dominantly removed by reduction as zerovalent metal and less by hydroxide precipitation. The main mechanism of zinc removal is based on the precipitation of hydroxide and co-precipitation on $Al(OH)_3$, which are less efficient processes. Influence of pH at metals removal depends on the MAlC behavior with pH change, nature of the metals and treatment time. After 15 min of the treatment, in the whole investigated pH range, removal efficiency of copper reached value as high as 90%, while the lowest efficacy at about neutral pH. In the same period, removal of zinc is much more affected by the initial pH and in acid and basic conditions, efficiency is small. The highest efficiency was at about neutral initial pH, contrary to copper. However, influence of pH declines with time and after 30 min it is much less while after 45 min almost negligible, because of pH leveling in all model wastewaters. The composite is amphoteric material and its reduction activity increases from neutral pH to acid and basic, which is the main factor determining copper removal efficiency. Opposite to copper, initial pH play obviously greater importance for zinc removal efficiency, thus it is the main factor for hydroxide formation. Increase of the initial concentration of metals decreases removal rates mainly because of saturation of the MAlC surface. In mixed solutions, copper as noble metal increases the MAlC activity and by that removal rate of Zn^{2+}. Efficacy of the MAlC treatment increases by increment of the flow rate, because it is mass-transport controlled process. Flow rate enhances probability of metal ion contact with composite, which is especially important for direct reduction. Because of that, with flow rate removal of copper increases faster than removal of zinc. All these results give indisputable evidence that presented spontaneous reduction–coagulation process, based on the micro-alloyed aluminium composite, can effectively reduce Cu^{2+} and Zn^{2+} ions to a very low level in different industrial wastewaters.

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