

Removal of chromium (VI) from water by micro-alloyed aluminium composite (MAIC) under flow conditions

A Lj Bojic*, M Purenovic and D Bojic

Department of Chemistry, the Faculty of Mathematics and Natural Sciences, University of Niš, Višegradaska 33, 18 000 Niš, Serbia

Abstract

This paper deals with Cr(VI) ion removal from water, by micro-alloyed aluminium composite (MAIC), under flow conditions. In a water environment the MAIC acts as a strong reducing agent. Dissolving it in water is accompanied by the generation of Al(III) ions and reduction of water to H₂, with OH⁻ ions. The final product is insoluble Al(OH)₃. A series of Cr(VI) model solutions, with initial pH ranging between 1 and 5, were treated in the original semi-flow system (SFS), which simulated flow conditions well. The results demonstrate a high MAIC efficacy, considering that at the end of the treatment, concentrations of Cr(VI) were below the maximal allowed concentrations for drinking water, in all model solutions. The MAIC mechanism of action is based mainly on processes of reduction and co-precipitation by Al(OH)₃, because Cr(VI) is removed from the water phase as metal chromium and insoluble Cr(OH)₃. Behaviour of the composite in water is under significant influence of pH, which affects its efficacy and mechanism of action. Therefore, the rate of Cr(VI) removal is greater at the beginning, decreasing towards the end of the treatment. Additionally, the ratio of [metal chromium]/[Cr(OH)₃] in precipitate, at the end of the treatment, decreases with increasing initial pH of the model solution. Application of the SFS significantly enlarges efficacy of the MAIC, compared to work under stationary conditions.

Keywords: chromium (VI) removal, wastewater, micro-alloyed aluminium, reduction, co-precipitation, flow conditions

Introduction

Chromium is present in the environment in both trivalent and hexavalent oxidation states. Cr(III) occurs naturally and is an essential micronutrient (requirement is 50 to 200 µg per day) that assists the body in metabolising sugar, protein and fat. Cr(VI) is usually of anthropogenic origin and rarely occurs naturally (Barceloux, 1999; Barnhart, 1997). Chromium-plating processes are the main source of Cr(VI) pollution. Cr(VI) is a skin and mucous membrane irritant and some of these hexavalent compounds produce an allergic contact dermatitis characterised by eczema (Hassmanova et al., 2000; Kanerva et al., 2000); it is also recognised as a pulmonary carcinogen (Barceloux, 1999; Hassmanova et al., 2000). Because of these potential health hazards the maximum level of Cr(VI) allowed in drinking water is 0.05 mgCr·L⁻¹ (*Standard Methods*, 1995). The remediation of Cr(VI)-contaminated industrial effluents is gaining great interest due to limitations in potable water supplies. The main strategies for Cr(VI) removal from wastewaters are precipitation as Cr(OH)₃ (Paterson, 1975; Cooney et al., 1992) and ion exchange (Tenorio and Espinosa, 2001). In addition, there are other options such as sorption onto various materials (Mesuere and Fish, 1992; Leinonen and Lehto, 2001; Selvi, 2001) and membrane filtration (Bohdziewicz, 2000; Alliane et al., 2001).

This study investigated a new treatment process for the removal of Cr(VI) from aqueous solutions by applying MAIC, under flow conditions. The composite consists of micro-alloyed aluminium

(MAI), coated over a thin iron wire. In aqueous solutions, it behaves like a strong reducing agent, which may affect various pollutants in water. Additionally, as a final product of the MAI, dissolution, water-insoluble Al(OH)₃ is produced, which may co-precipitate pollutants and their degradation products from the water phase (Bojic, 1997; Purenovic et al., 1998; Novakovic et al., 1998).

Previous studies (Bojic, 1997; Purenovic et al., 1998; Novakovic et al., 1998), which deal with purification of different wastewaters, show great MAIC efficacy. After water treatments, concentrations of pollutants were reduced for several logs in a relatively short period, and in many cases, they were below the maximum allowed concentrations. The major factors significant for MAIC efficacy are treatment time, the total area of applied composite wires and water convection. The influence of convection is obvious from previous studies which showed that composites have greater efficacy under flow conditions than under stationary conditions (Bojic et al., 2001; Bojic, 2002). Flow systems, applied in some experiments, were massive and impractical for laboratory work and therefore in this study an original semi-flow system was designed, which simulates flow conditions in small spaces (Bojic et al., 2001; Bojic, 2002). Mechanisms of MAIC action on various inorganic and organic compounds (Bojic, 1997; Purenovic et al., 1998; Novakovic et al., 1998), as well as micro-organisms in water (Bojic et al., 2001; Bojic, 2002), were also investigated. It is mainly based on reduction and hydrolysis. It is important to emphasise that in all prior studies no undesirable by-products were found in the water phase after treatment.

The results obtained in this work show that the MAIC treatment of Cr(VI) wastewaters is very efficient, simple and does not acquire any pretreatment, such as pH correction.

* To whom all correspondence should be addressed.

☎+381 64 229-36-40; fax:+381 18 533-014; e-mail: bojic@bankerinter.net

Received 16 January 2004; accepted in revised form 5 March 2004.

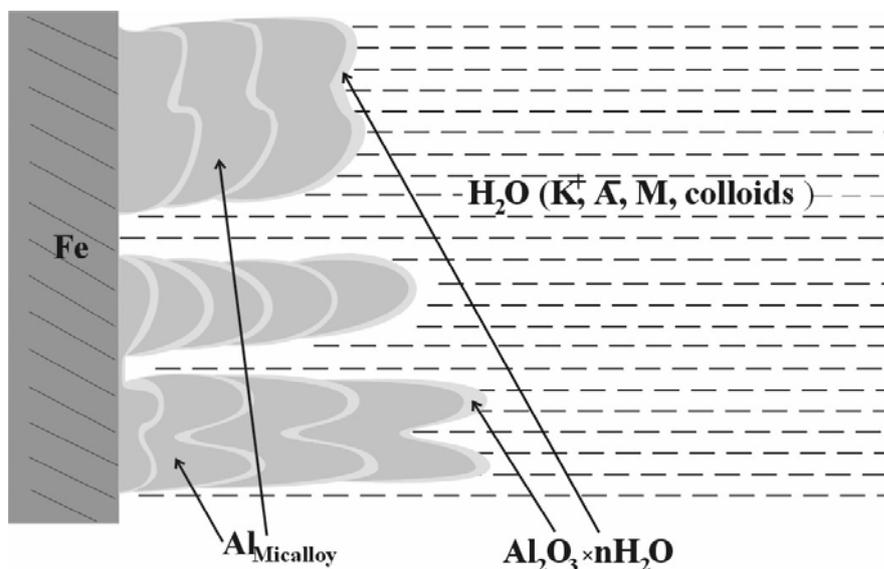


Figure 1
A model of the MAIC structure in aqueous medium

Experimental

Chemicals

The experiments were carried out with the model solutions, the composition of which correlates with the composition of effluent waters from a chromium-plating industry. These wastewaters usually contain Cr(VI) ion in concentration ranges between 25 and 300 mgCr·ℓ⁻¹. Considering that the pH of a chromic plating bath is between 0 and 1, because of the presence of sulphuric acid, pH of the chromium-plating wastewaters varies between 2 and 4 (Lowe, 1970; Paterson, 1975).

The model solutions were prepared by diluting 1.00 gCr·ℓ⁻¹ stock solution of Cr(VI), and adjusting the pH with diluted H₂SO₄, pH-metrically. A stock solution was obtained by dissolving the exact quantity of K₂Cr₂O₇ in 1.00 ℓ of deionised distilled water. The series of model solutions, containing 150 mgCr·ℓ⁻¹ of Cr(VI), with pH 1.00 (I), 2.00 (II), 3.00 (III), 4.00 (IV), and 5.00 (V), were prepared.

All chemicals were obtained from Merck (Darmstadt, Germany), unless otherwise indicated.

MAIC composite

The MAI is a new material with different properties compared to pure aluminium. It is prepared by micro-alloying 99.8% purity aluminium with: Sn, Ga and Bi (Purenovic, 1978; Purenovic, 1992). After micro-alloying, the obtained material was analysed by flame atomic absorption spectroscopy (FAAS) using a VARIAN SpectrAA-20 (Mulgrave, Victoria, Australia), and amounts of metals found were: 0.105% Sn, 0.098% Ga and 0.040% Bi.

By micro-alloying the oxide layer of aluminium, it becomes porous and permeable for ions, because of the many defects in the crystal lattice due to different dimensions and charges of micro-alloyed elements, related to Al³⁺ (Despic et al., 1976; Purenovic, 1978). Micro-alloyed components generate defects in a metal structure (interstitials and vacancies in crystal lattice) and an imbalance in the charge distribution, as a result of many micro-galvanic cells. These defects decrease energy barriers for transport of Al³⁺ ion from metal to oxide layer, and O²⁻ ion from oxide to metal. An after-effect is an increase in ionic and electronic conductivity by 10⁴ to 10⁶ times, and increase of corrosion rate for almost the same order of magnitude (Purenovic, 1978; Purenovic, 1992). Accordingly, the stationary potential of the MAI is negative, about

-1.5 V/SCE (saturated calomel electrode), and this makes the MAI chemically much more reactive than pure aluminium. A basic characteristic of the MAI is its very negative stationary potential, compared to pure aluminium, and because of that its first usage was anodic anti-corrosion protection of iron (Purenovic, 1980).

The composite was made by metalising an iron wire (mesh 1.2 x 1.2 mm, Ø 0.6) with MAI, by means of a special gas burner (Metco, USA) (Purenovic, 1992). The obtained material has an amorphous surface area, the micro-porosity being in the form of fish scales, and offers convenient sites and a large specific surface area for the adsorption of different ions, molecules and colloids dissolved in water. MAIC in aqueous medium is presented in Fig. 1.

Besides many local micro-galvanic cells in MAI, there is also a macro-galvanic cell, Fe | Al_{Micalloy} (Fig. 1). The MAI and iron composite (author to check) additionally decreases the potential of MAI, which leads to enhancement of the dissolution rate and anode activity (Despic et al., 1976; Purenovic, 1992).

The influence of the composite on water pollutants is based on its spontaneous reaction with water, similar to the reaction of alkaline and earth metals (Purenovic, 1992; Bojic, 1997). The main process on micro-anodes is dissolution of aluminium with the generation of Al(III) ions, by oxidation of Al via Al⁺, and Al²⁺ stages. The main process on micro-cathodes is reduction of water to H₂, via H[·] stage, in the process releasing OH⁻ ions (Cotton and Wilkinson, 1972; Purenovic, 1978). Every particle, besides water molecules, which come to the surface of the composite, may become a participant in the many chemical processes (reduction, hydrolysis, addition). Al(III) and OH⁻ ions form insoluble aluminium-hydroxide. It coagulates to form a gelatinous, voluminous colloidal precipitate with a distinctly developed surface area, a common reagent for the co-precipitation (Voyutsky, 1978). Usually, low amounts of pollutants, as products of their chemical degradation by the MAIC, become co-precipitated by the aluminium-hydroxide during the treatment and removed from the water phase (Purenovic, 1992; Bojic, 1997; Purenovic et al., 1998; Novakovic et al., 1998; Bojic, 2002).

Laboratory equipment

The treatments of the MAIC model solutions were performed in the original semi-flow system (Bojic, 2002). Equipment, shown schematically in Fig. 2, consisted of several parts. The main bath (MB) made of high-density polyethylene, held a volume of 10.0 ℓ

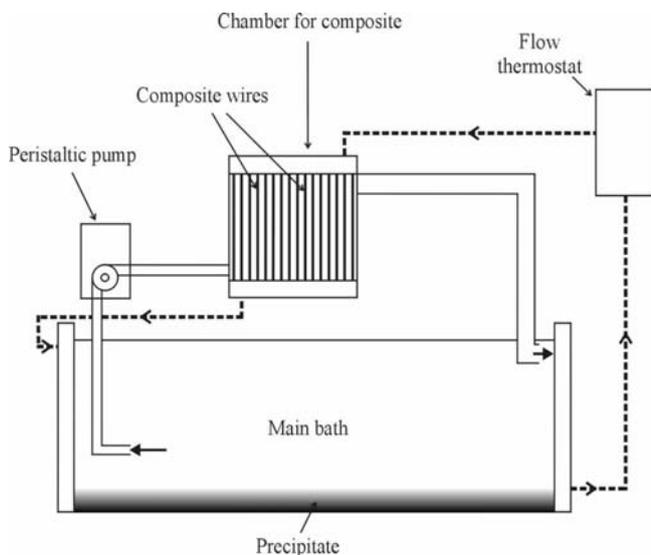


Figure 2
Schematic diagram of the original semi-flow system

solution, while the composite chamber (CC), also of high-density polyethylene, had a volume of 1.0 L. Sixteen composite wires, dimension 100 x 100 mm, placed to the perpendicular direction of water flow in CC, and the peristaltic pump for injecting of solution from MB to CC, with flow rate maintained at 90 L·h⁻¹.

CC was located at 50 mm above the water level in the MB (Fig. 2). Its frontal side was connected, at the bottom, with a peristaltic pump by means of polyethylene pipe (Ø20 mm). The horizontal end of the tube entering the peristaltic pump was immersed at about 70 mm from the bottom end of the MB (Fig. 2), to prevent plugging of Al(OH)₃ precipitate formed during the treatment. Solutions from the CC were continuously returned to the MB by overflow pipe (Ø40 mm), which formed a closed loop (Bojic, 2002). The temperature was kept constant by flow thermostat, connected to the water jackets of the MB and the CC.

With a limited number of composite wires in a relatively small area, normal flow conditions were simulated by passing the model solution through the composite chamber a number of times. In comparison, the flow system can be presented as a long CC, with water flowing over it continuously. Such equipment is much larger than the SFS, and comprises a few hundred composite wires. The requisite volume of solutions has to be about 40 to 50 L, because of the necessity of the initial chemical "activation" of wire surfaces, and filling of the system with fluid. On the other hand, the SFS is more efficient than stationary conditions (Bojic, 1997; Novakovic et al., 1998; Purenovic et al., 1998), where the composite wires are simply immersed in the solution contained in the vessel.

Experimental procedure

8.0 L of each model solution was equilibrated at 20°C, and transferred to the main bath. After taking the zero probes (time 0 min), the peristaltic pump and thermostat were run. Samples of the model solutions for analysis were withdrawn every 15 min from the MB by pipette, transferred to flasks with glass stoppers and left to stand for the Al(OH)₃ to precipitate. The MAIC treatment time was determined in terms of the nature of each pollutant and its initial concentration, and it was set to 120 min. During the treatment, pH was monitored, by pH-meter Corning Checkmate Modular Testing System (Corning, USA), with a combined electrode. All experiments were performed in triplicate on the same model solution.

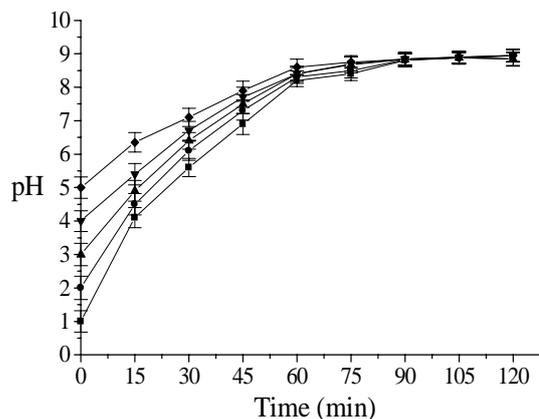


Figure 3
Monitoring of pH in the model solutions with initial pH: 1.00 (■), 2.00 (●), 3.00 (▲), 4.00 (▼) and 5.00 (◆), during the treatment by the MAIC, in the semi-flow system at 20°C. Error bars represent the standard deviation of mean values of the triplicate sample.

At the end of the treatment, the composite wires were removed from the CC. It was noted that black amorphous powder of reduced metal chromium, had been deposited on the surface during the treatment. Wires were gently washed with deionised distilled water and their surface layer was dissolved in a minimal volume of diluted HCl. After removal of the wires, a small amount of concentrated HCl was added to the solution and it was boiled for couple of minutes in order to dissolve of larger particles totally. The resultant solution was diluted, and chromium was determined.

The total amount of voluminous Al(OH)₃ precipitate formed during the treatment in the MB and the CC was collected, decanted from the water phase and weighed. After that, the precipitate was homogenised by stirring, and sample aliquots of 25.0 mL were taken. Sampled precipitate was weighed and dissolved in the NaOH. The solution was filtered through black ribbon filter paper and analysed for Cr(III) and Cr(VI). Black powder residue at the filter paper was treated with HCl and heated. Chromium was determined in solution thus obtained.

Analytical methods

Chromium(VI) was determined in the model solution samples and in the dissolved Al(OH)₃ precipitate by means of the chelation-extraction method for hexavalent chromium according to Method 218.4 described in EPA (1983). The analyses were performed by flame atomic absorption spectroscopy using a VARIAN SpectrAA-20, in an air-acetylene flame.

In solutions obtained by dissolving of Al(OH)₃ and composite wires, Cr(III) was determined by FAAS, applying Method 218.1 (EPA, 1983), in a nitrous oxide-acetylene flame.

Results and discussion

The results of pH monitoring in the of Cr(VI) model solutions, with initial pH: 1.00, 2.00, 3.00, 4.00 and 5.00, during the treatment by the MAIC in the semi-flow system, are shown in Fig. 3.

At the start of the treatment, the pH of model solutions rapidly increased (Fig. 3). After that, the pH gradient decreased, and after about 60 min, the pH of all the model solutions became almost equal (Fig. 3). In the second half of the treatment, there was no significant pH variation (pH was about 9).

The pH changes of the model solutions during the treatment were a function of their initial value. This dependence is shown in

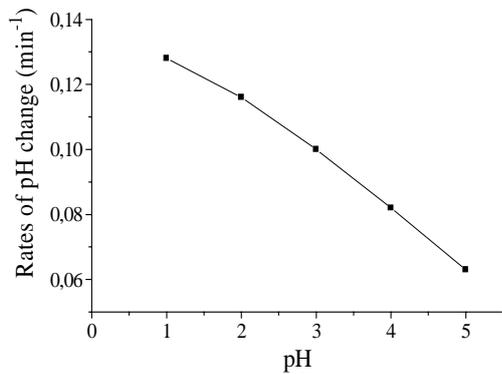


Figure 4

The rates of pH change over the period of the treatment from 0 to 60 min, as a function of initial pH of model solutions

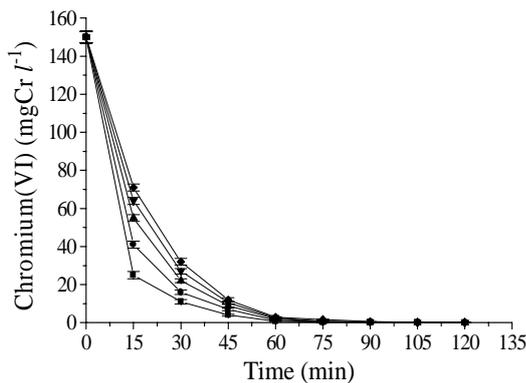


Figure 5

Changes of Cr(VI) concentration in the model solutions with initial pH: 1.00 (■), 2.00 (●), 3.00 (▲), 4.00 (▼) and 5.00 (◆), during the treatment by the MAIC, in the semi-flow system at 20°C. Error bars represent the standard deviation of triplicate sample means values

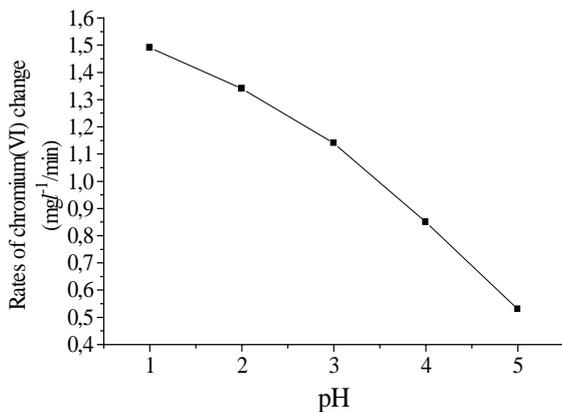


Figure 6

The rates of change of Cr(VI) concentration in period of the treatment from 0 to 60 min, in function of initial pH of model solutions

Fig. 4, as a rate of pH change as a function of initial pH, over the period of treatment from 0 to 60 min.

The rates of pH change significantly decreased with increasing initial pH. However, after 60 min the pH values of all model solutions became equal, even though the pH varied considerably at the start (from 1 to 5). Figure 4 shows that the rate of pH change for

model Solution I was twofold greater than for Solution V, under given conditions.

Results shown are in accordance with findings from previous studies of MAIC treatments (Purenovic, 1992; Bojic, 1997; Purenovic et al., 1998; Novakovic et al., 1998; Bojic et al., 2001; Bojic, 2002), where, after a particular period of time, the pH of solutions always became about 9, irrespective of initial pH. The MAI spontaneously reacts with water owing to very negative reduction potential in contrast to a pure metal, and this process is intensified by acids and bases. After neutralisation, Al(III) and OH⁻ ions appeared in almost stoichiometrical amounts, because of continual formation of insoluble Al(OH)₃, and pH became constant.

The results of changes of Cr(VI) concentration in model solutions with initial concentration of Cr(VI) 150 mg·l⁻¹ and pH: 1.00, 2.00, 3.00, 4.00 and 5.00, during the MAIC treatment in the semi-flow system, are shown in Fig. 5.

Figure 5 shows that at the beginning of the treatment in all model solutions, concentrations of Cr(VI) rapidly decreased, and after about 60 min total concentration decay was about 3 orders of magnitude. During the second half of the treatment, the next 60 min, change of Cr(VI) concentration was significantly smaller.

The rates of change of Cr(VI) concentration in function of pH, for the period 0 to 60 min, are shown in Fig. 6.

With decreasing initial pH, the rates of change of Cr(VI) concentration regularly increased. Acidity of model solution increased the MAI dissolution and reduction efficiency of the composite (Bojic, 1997; Purenovic et al., 1998). Because of that, in the first half of the treatment, efficacy of the composite was greater in model solutions with lower pH. Considering that the pH of model solutions became equal after 60 min (Fig. 3), efficacy of the composite became equal, too (period from 60 to 120 min, Fig. 5). Concentrations of Cr(VI) in model solutions at the end of the treatment by the MAIC are shown in Table 1, as an average with standard deviation.

Model solution	Cr(VI) ± SD [mgCr·l ⁻¹]
I	0.007 ± 0.003
II	0.021 ± 0.008
III	0.03 ± 0.011
IV	0.036 ± 0.014
V	0.04 ± 0.012

Results in Table 1 demonstrate that final concentrations of Cr(VI) at the end of the treatment were very low in all model solutions. Their values depended on initial pH, and it was shown that the concentration difference between model Solutions I and V was about one order of magnitude.

Analysis of the surface area of the composite wires after the treatment showed the presence of metal chromium, deposited in the form of a black amorphous powder. Amounts of metal chromium on composite wires are shown in Table 2. Averages with standard deviation are shown.

Presented results reveal that the amounts of metal chromium deposited on the composite wires after treatment were rather low.

Model solution	Chromium \pm SD [mg]
I	17.4 \pm 2.1
II	17.1 \pm 1.8
III	16.6 \pm 2.0
IV	17.5 \pm 1.8
V	15.8 \pm 1.4

By comparing the results, small differences were noted among model solutions, which indicate that deposition of chromium was not affected by initial pH.

Testing of $\text{Al}(\text{OH})_3$ precipitate showed that it comprised major amounts of Cr(VI), which were removed during the treatment. In precipitate, the chromium was in the reduced forms, as Cr(III) and metal chromium. However, a small amount of Cr(VI), was also co-precipitated during the treatment.

The amounts of chromium, Cr(III) and Cr(VI) in the $\text{Al}(\text{OH})_3$ precipitate are presented in Table 3. Averages with standard deviation are shown.

Model solution	Metal chromium \pm SD [mg]	Cr(III) \pm SD [mgCr]	Cr(VI) \pm SD [mgCr]
I	903 \pm 12.5	273 \pm 8.5	8.5 \pm 1.6
II	697.5 \pm 10.4	432 \pm 9.5	14.4 \pm 2.2
III	541.5 \pm 10.5	591 \pm 12.0	18.0 \pm 2.3
IV	408 \pm 9.5	712.5 \pm 12.4	23.6 \pm 2.5
V	316.5 \pm 8.4	802 \pm 14.4	27.4 \pm 2.1

It can be noted that the amount of each chromium species in $\text{Al}(\text{OH})_3$ precipitate depends on the initial pH of the model solution. With increasing initial pH, the amount of metal chromium in the precipitate decreases, and the content of Cr(III) content increases. Content of Cr(VI) in a precipitate is two orders of magnitude lower than metal chromium and Cr(III), and it increases with initial pH.

The presence of metal chromium and Cr(III)-hydroxide in precipitate indicates that the mechanism of removal of Cr(VI) from water phase is based mainly on reduction. This reduction process is especially intensified by oxidation characteristics of Cr(VI), the redox potential of which is +1.33 V (Rieger, 1987). It is presumed that reduction of Cr(VI) occurs on the very surface of the composite wires, while the water phase passes through the composite chamber.

The assumption is that at the beginning of each treatment, when reduction activity of the composite is greater, chromium is mainly removed from the water phase in totally reduced form – metal chromium. Considering that the MAI was continuously dissolved during the treatment, with permanent regeneration of its surface, reduced chromium (amorphous black powder) was co-precipitated

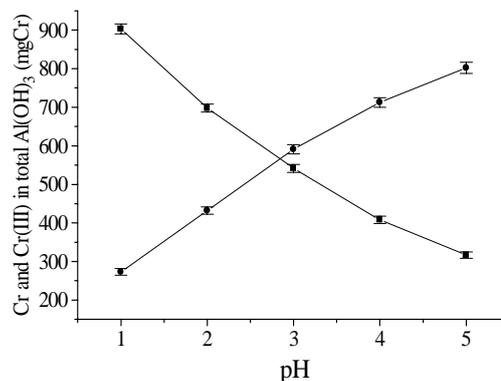


Figure 7
Amounts of metal chromium (■) and Cr(III) (●) in $\text{Al}(\text{OH})_3$ precipitate at the end of the treatment as a function of initial pH of model solution

by $\text{Al}(\text{OH})_3$. That is the reason why small amounts are found on the composite wires at the end of each treatment.

The amount of elementary chromium deposited during the treatment, is dependent on the initial pH of the model solution. Decrease of metal chromium with increasing initial pH is graphically shown by curve (■) in Fig. 7, based on the results shown in Table 3.

The residual part of Cr(VI) from the water phase was reduced to Cr(III), precipitated in the form of $\text{Cr}(\text{OH})_3$. This can be explained by the fact that Cr(III) appears later during the treatment, which is multiple related to pH value of environment. Initially, composite reduction activity decreases with increasing pH. The second phenomenon is the increase of concentration of the OH^- ion, which reacts with Cr(III) and forms insoluble $\text{Cr}(\text{OH})_3$. Additionally, with increasing OH^- ion concentration, the amount of colloid $\text{Al}(\text{OH})_3$, co-precipitation reagent, increases because concentrations of OH^- and Al^{3+} ions exceed the solubility product of $\text{Al}(\text{OH})_3$ (Cotton and Wilkinson, 1972; Martin, 1991).

All the above-mentioned phenomena interrupt reduction of Cr(VI) during the Cr(III) stage, because of the formation of very stable, insoluble $\text{Cr}(\text{OH})_3$, which cannot contact with composite wires. Figure 7 shows that the amount of chromium removed from water phase as $\text{Cr}(\text{OH})_3$ regularly increased with initial pH of model solutions.

Amounts of Cr(VI) co-precipitated by $\text{Al}(\text{OH})_3$ were rather low in all model solutions, and depended on initial pH. Start of Cr(VI) co-precipitation was accompanied by sufficient formation of colloid $\text{Al}(\text{OH})_3$. Those conditions were achieved earlier in model solutions with higher initial pH, and necessary periods were from 25 to 40 min (Fig. 3). Considering that, at the moment when co-precipitation of Cr(VI) had started (Fig. 5), its concentration was greater in model solutions with higher initial pH, the outcome was an increase of Cr(VI) in $\text{Al}(\text{OH})_3$ precipitate with initial pH (Table 3).

In contrast with a previous study (Purenovic et al., 1998), which had dealt with removal of Cr(VI) from wastewaters under stationary conditions, the results obtained in this work by applying semi-flow systems showed major efficacy of the MAIC. Purenovic et al. (1998) had treated effluents discharged by the chromium-plating industry. Experiments were done on a series of wastewater samples, with adjusted Cr(VI) concentration to 145.0 $\text{mgCr}\cdot\ell^{-1}$, pH between 1 and 11 and sample aliquots of 1.0 ℓ . The samples were subjected to four composite wires, under stationary conditions, over a period of 60 min. The results are shown in Fig. 8.

Purenovic et al. (1998) used 0.035 $\text{mgCr(VI)}\cdot\text{mm}^{-2}$ of geometric surface areas of wires. The same conditions were used in this

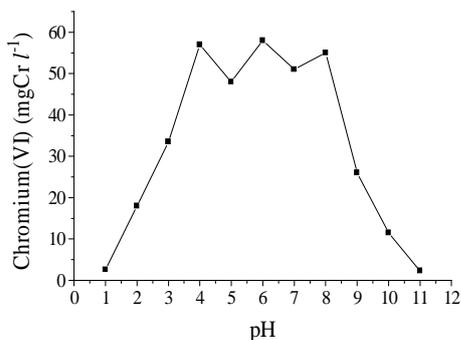


Figure 8

Cr(VI) concentration after 60 min of the MAIC treatment in stationary conditions, in function of pH. Initial concentration of Cr(VI) in all samples was 145.0 mgCr·L⁻¹ (Purenovic et al., 1998)

study as well. Comparing the results in Figs. 5 and 8, it is shown that the semi-flow system achieved greater efficacy of the MAIC. In 60 min period in stationary conditions, reduction of Cr(VI) concentration was one log or less; in contrast to this, in the SFS reduction it was about 3 logs.

Comparing the SFS with stationary conditions, where pollutants make contact with the composite surface only by diffusion, the water continually “filters” through the composite wires, which increases the probability of contact between a pollutant and the composite. The convection in the semi-flow system accelerates diffusion of Al(III) and OH⁻ ions from the wire surface, and accordingly dissolution of the MAI, which additionally increases the composite activity.

Conclusions

The results of the study presented here show that the micro-alloyed aluminium composite, used in the semi-flow system, is a powerful device for the removal of Cr(VI) from wastewaters, over a wide range of initial pH.

Behaviour of composites in an aqueous environment is significantly influenced by pH, due to the negative reduction potential as well as amphoteric characteristics of micro-alloyed aluminium. The pH affects both composite efficacy and mechanism of action. During the treatment, pH of solutions increases to a specific value, and after that it becomes constant. It could be said that composite and water represent a specific buffer system, which may adjust the pH of any aqueous solution to a value of about 9.

Total decline of Cr(VI) concentration after 120 min of the MAIC treatment is appreciable in all model solutions, and it is about 5 logs. The rate of change of Cr(VI) concentration is the highest at the start of treatment in all model solutions, because of low pH. During the treatment, the rate of change declines, as composite efficacy decreases, and for a long period, change of Cr(VI) concentration is in the range of one log. Differences in final concentrations of Cr(VI) between model solutions are about one order of magnitude, which illustrates the influence of initial pH on the treatment efficacy.

Considering that Cr(VI) removed from the water phase was found in Al(OH)₃ in the form of metal chromium and Cr(III)-hydroxide, the mechanism of Cr(VI) removal is mainly based on reduction. Differences in the ratio of metal chromium and Cr(III) amounts in Al(OH)₃ between model solutions, indicate that, in the case of Cr(VI), initial pH influences the mechanism of the composite action, far more than its efficacy. Cr(VI) was present in very low

amounts in the precipitate, and that fact is very important for further handling of the precipitate.

After 120 min of the treatment, concentrations of Cr(VI) in all model solutions were below maximum allowed concentrations for drinking water (0.05 mgCr·L⁻¹), and after 70 to 80 min, depending on initial pH, Cr(VI) concentrations were about those allowed for rivers of Class III (0.5 mgCr·L⁻¹).

The presented semi-flow system enables the total volume of model solution to pass through the composite chamber multiple times, which is a simplified simulation of the flow conditions. The SFS increases the efficacy of the MAIC considerably, compared to the stationary conditions.

The pH of the water phase at the end of the composite treatments is usually about 9, and under these conditions solubility of aluminium is great (Martin, 1991). Therefore, it is always necessary to adjust the pH of purified water to about 6.5, and to filter it to reduce Al concentration to within the allowed range, in order to prevent contamination of the environment.

Acknowledgements

This study was supported by the Ministry of Science and Technology of Serbia and Montenegro, Materials and Chemical Technology: No 0279.

References

- ALLIANE A, BOUNATIRON, CHERIF AT and AKRETCHE DE (2001) Removal of chromium from aqueous solution by complexation-ultrafiltration using a water-soluble macroligand. *Water Res.* **35** (9) 2320-2326.
- BARCELOUX DG (1999) Chromium. *J. Toxicol. Clin. Toxicol.* **37** (2) 173-194.
- BARNHART J (1997) Occurrences, uses, and properties of chromium. *Regul. Toxicol. Pharmacol.* **26** (1) 3-7.
- BOHDZIEWICZ J (2000) Removal of chromium ions(VI) from underground water in the hybrid complexation-ultrafiltration process. *Desalination* **129** 227-235.
- BOJIC A (1997) Physicochemical Phenomena at Heterogenic Spontaneous Electrocatalysis of Some Organic and Inorganic Compounds in Aqueous Solutions by Applying The Solid Metal Catalyst Based on Microalloyed Aluminium. M.Sc. Thesis, Department of Chemistry, University of Niš (in Serbian). 124 pp.
- BOJIC A (2002) The Mechanism of Influence of Electrochemically Active Microalloyed Aluminium Based Composite on Microorganisms in Aqueous Medium. Ph.D. Thesis, Department of Chemistry, University of Niš (in Serbian). 114 pp.
- BOJIC A, PURENOVIC M, KOCIC B, PEROVIC J, URSIC-JANKOVIC J and BOJIC D (2001) The inactivation of *Escherichia coli* by microalloyed aluminium based composite *Facta Universitatis.* **2** 115-124.
- COONEY E, LUO B, PATTERSON JW and PETROPOULOU C (1992) Toxicity reduction methodologies. In: Ford DL (ed.) *Water Quality Management Library* Vol. 3. Lancaster, PA: Technomic. 109-181.
- COTTON AF and WILKINSON G (1972) *Basic Inorganic Chemistry*. John Wiley and Sons, New York.
- DESPIC A, DRAIC D, PURENOVIC M and CIKOVIC N (1976) Electrochemical properties of aluminium alloys containing indium and thallium. *J. Appl. Electrochem.* **6** 529-536.
- EPA (1983) Methods for chemical analysis of water and wastes. In: William A Telliard (ed.) *Office of Water Test Methods and Guidance*. US EPA, Washington, DC (on CD-ROM).
- HASSMANOVA V, VANECKOVA J and BOUSOVA K (2000) Occupational diseases caused by chromium and its compounds. *Acta. Med.* **43** 33-36.
- KANERVAL, JOLANKIR, ESTLANDER T, ALANKO K and SAVELA A (2000) Incidence rates of occupational allergic contact dermatitis caused by metals. *Am. J. Contact. Dermat.* **11** (3) 155-160.

- LEINONEN H and LEHTO J (2001) Purification of metal finishing waste waters with zeolites and activated carbons. *Waste Manage. Res.* **19** (1) 45-57.
- LOWE W (1970) *The Origin and Characteristics of Toxic Wastes With Particular Reference to the Tetal Industries*. Water Pollution Control, London. 270-280.
- MARTIN RB (1991) Fe³⁺ and Al³⁺ hydrolysis equilibria. *J. Inorg. Biochem.* **44** 141-147.
- MESUERE K and FISH W (1992) Chromate and oxalate adsorption on goethite 1. Calibration of surface complexation models. *Environ. Sci. Technol.* **26** 2357-2364.
- NOVAKOVIC M, PURENOVIC M, PEROVIC J, MILJKOVIC M, RANĀIC S and BOJIC A (1998) Waste water refinement by the solid metal catalyst. *Acta. Biol. Iug.* **33** 363-366.
- PATERSON JW (1975) *Wastewater Treatment Technology*. Ann Arbor Science, Michigan. 43-58.
- PURENOVIC M (1978) Influence of Some Alloying Components on Electrochemical Behaviour of System Al-O Layer Electrolyte. Ph.D. Thesis, Faculty of Technology, University of Belgrade (in Serbian). 187 pp.
- PURENOVIC M (1980) Yu-Patent 1334/80.
- PURENOVIC M (1992) Yu-Patent 669/92.
- PURENOVIC M, BOJIC A, STANISAVLJEVIC M and VELJKOVIC N (1998) Chrome waste water treatment in wide pH range on new solid catalyser. *2nd Intl. Conf. "Advanced Wastewater Treatment, Recycling and Reuse"*. Milan, Italy, September 14-16. 927-930.
- RIEGER PH (1987) *Electrochemistry*. Prince-Hall, New Jersey.
- SELVI K, PATTABHI S and KADIRVELU K (2001) Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon. *Bioresour. Technol.* **80** (1) 87-89.
- STANDARD METHODS (1995) *Standard Methods for the Examination of Water and Wastewater* (19th edn.) American Public Health Association, Washington, DC.
- TENORIO JA and ESPINOSA DC (2001) Treatment of chromium plating process effluents with ion exchange resins. *Waste Manage.* **21** (7) 637-642.
- VOYUTSKY S (1978) *Colloid Chemistry*. MIR, Moscow.
-

