REMOVAL THE HEAVY METAL IONS FROM ACIDIC MINE DRAINAGE GENERATED AT "ROSIA MONTANA" GOLD MINE (ROMANIA) BY USING CYPRINUS CARPIO SCALE AS BIOSORBENT

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ABSTRACT: Biosorption of heavy metals by different waste materials is one of the treatments that has emerged as an environmentally friendly method for removing metals from aqueous solutions. As previous studies reported the potential of chemical pre-treatments to enhance the activity of fish scales in removing heavy metals from synthetic wastewater, in the present study, the biosorptive potential of Cyprinus carpio scales pre-treated with 1 M NaCl, 0.1 M NaOH and 2% soluble potassium salts of humic acids for the removal of Fe3+, Mn2+ and Zn2+ from real acidic mine drainage (AMD) was investigated. Before and after the biosorption process, the biosorbent was characterised using scanning electron microscopy - energy-dispersive X-ray spectroscopy (SEM-EDX). Experiments to determine the effect of the chemical pre-treatment agent on the sorption process were performed. The results showed that this inexpensive biowaste offers great potential for the removal of metal ions since a solid:liquid ratio of 1:50 (g:mL) was sufficient to reduce the Zn concentration below the values established by Romanian legislation, after 240 min of stirring. In the investigated experimental conditions, about 100 %, 82.3 % and 98.08% of iron, manganese, and zinc ions were removed from AMD solution after 240 min of contact with the finest-grained Cyprinus carpio scales sample pre-treated with 0.1 M NaOH.

Keywords: heavy metals; fish scales; acid mine drainage; biosorption; SEM-EDX;

1. Introduction

Acid mine drainage (AMD) is an unavoidable by-product of mining and sulfide-bearing mineral processing which have a very low pH and contains high concentrations of sulfate ions and dissolved (toxic) heavy metals (i.e. Zn, Mn, Cu, Pb, Cr, Ni, Cd). AMD greatly affects the receiving environment [1, 2] mainly by altering the ambient pH [3] and heavy metal accumulation. Consequently, the reduction of the heavy metal concentrations from AMD has become a significant issue for environmental experts.

Different methods have been devised to remove heavy metals from AMD. Neutralization, precipitation [4], electrocoagulation [5], membrane separation [6, 7], microbial treatment [8, 9], constructed wetland [10], and adsorption using synthetic and natural adsorbents [11] methods are the most practical method addressed in the literature.

To achieve sustainability and circular economy and to provide value to waste materials which is encouraged the world over, in the last years, a large number of investigations have been conducted on the use of industrial and agricultural waste products as low-cost, easily available potential adsorbents for the removal of pollutants (heavy metals, dye, anions etc.) from the wastewaters. Investigated materials include animal bones, fish bones and scales, crab and arca shells, egg and nut shells, rice husks, potato and mandarin peels, starch etc. [12, 2, 13].

Fish scales are a waste material with no other competitive use. Although some part of fish scales has been used for collagen, chitin and derivatives extraction [14, 15] still waste generation rate is too high. The storage of such an amount of waste in the environment leads to serious environmental and health problems along with undesirable odor.

To overcome the environmental issues and for the full use of fish scale biomass for purposes of high-commercial value, various studies investigated the performance of several fish scales-types for the removal of heavy metal ions from synthetic solutions, with most of the reported removal efficiencies lying above 50% [16-24]. Our previous investigation also confirmed that Cyprinus carpio fish scales can remove heavy metals from acidic mine drainage generated at the "Ro ia Montană" gold mine with good performances.

As previous literature studies reported that fish scale biomass chemically treated with alkali (NaOH) or acids (HCl) showed comparatively better removal efficiency than raw fish scales due to the removal of the unwanted lipids and proteins from the biomass surface that disguise the necessary reactive site for metal ions adsorption [25], this research will explore the unexploited property of the Cyprinus carpio fish scales pre-treated with 1 M NaCl, 0.1 M NaOH and 2% soluble potassium salts of humic acids as a new biosorptive material for the removal of Fe, Mn and Zn ions from acidic mine drainage generated at the "Ro ia Montană" gold mine from Romania. The soluble potassium salts of humic acids were selected as pre-treatment agents because of their reported ability to mobilize, neutralize, and remove heavy metals through complex formation with heavy metals from soil [26]. The influence of several parameters such as chemical pre-treatment of the biosorbent samples, particle size, and the contact time with acidic mine drainage was investigated. To investigate the morphological properties of the fish scales and to estimate their chemical composition, SEM and EDX analyses were performed before and after the contact with the acidic mine drainage.

2. Materials and methods

2.1. Study area and acidic mine drainage sample

The studied mining perimeter is located in the Apuseni mountains (Romania) and comprises as main exploitation "Rosia Montana" gold mine.

The "Rosia Montana" gold mining perimeter falls within the so-called "Transylvanian Gold Quadrangular" which includes the mining perimeters of Deva, Brad, Zlatna, and Caraciu [27]. Intensive extraction of ores rich in gold and silver performed in the eighteenth and nineteenth centuries caused severe problems related to the contamination of the soil, water, and vegetation with metalloids and heavy metals. For biosorption experiments, an actual acidic mine drainage (AMD) sample was collected from "Ro ia Montană" gold mining perimeter. The pH of the sample was measured on-site using a portable pH meter (Hanna instruments).

The chemical composition of the AMD was determined in laboratory by X-ray fluorescence spectrometry using a Quant'X ARL spectrometer (Thermo Scientific, USA) and the results are summarized in Table 1 (average values are presented).

The water drainage collected from "Ro ia Montana" gold mine have a very low pH (2.8) and the heavy metal concentrations are significant. The concentrations of the zinc, iron, manganese, copper, cadmium, and nickel ions in the acidic mine drainage exceed more than 2 to 56 times the maximum consent limits established by Romanian regulatory standard [28]. Since this acidic mine drainage is disposed of without any remediation treatment into the environment posing threats to the nearby ecosystem, it is obvious that it should be collected and treated.

Table 1. Chemical composition of the AMD sample collected from "Roşia Montana" gold mine

Element	Unit	Value	Maximum consent limits*
Fe	mg L^{-1}	201.5	5
Mn	mg L^{-1}	56.5	1
Zn	mg L^{-1}	17	0.5
Cu	mg L^{-1}	1.05	0.1
Cd	mg L^{-1}	4.65	0.2
Ni	mg L^{-1}	1.15	0.5
Ca	mg L^{-1}	221.5	300

2.2. Biosorbent sample

Waste fish scales used in biosorption experiments come from Cyprinus carpio grown in the Danube (Romania) and were collected from a local market. The fish scales were soaked in tap water for 24 hours and washed with distilled water several times to remove impurities from their surface. Then, the fish scales were dried at 60 € for about 4 hours. The dried fish scales were cut into small pieces of 5-7 mm and chemically treated to improve the efficiency of heavy metals uptake using different reagents, namely NaOH, NaCl, and soluble potassium salts of humic acids. For chemical pre-treatment, a quantity of 5 g of fish scales was soaked, for 2.5 hours under continuous stirring at 500 rpm, in 100 ml of 0.1M NaOH, 1M NaCl, and a solution containing 2% soluble potassium salts of humic acids, respectively. Afterwards, pre-treated fish scales were dried at 60 € till constant mass.

2.3. Surface characterization by SEM-EDX

The morphological characteristics of pre-treated fish scales, before and after the contact with the acid mining drainage water were determined using TM4000plus II scanning electron microscope (Hitachi, Japan) with a tungsten filament, at different acceleration voltages (15 kV and 20 kV) and magnifications (100x and 3000x). The elemental analysis of the samples was performed using a liquid nitrogen-free energy-dispersive X-ray mapping detector (Oxford Instruments, UK).

2.4. Batch biosorption experiments and metal analysis

The experiments were performed in the batch mode adsorption process at room temperature and constant agitation speed (500 rpm). A quantity of 2 g of chemically pre-treated fish scales were put in contact with 100 mL AMD for 240 minutes.

During the first hour in which the biosorbent was in contact with the mine water drainage sample, under continuous stirring, supernatants were extracted with a micropipette at 15-minute intervals. Then, in the next 3 hours, supernatants were extracted at 60-minute intervals. The separation of the liquid and solid phases was carried out by filtration process using filter papers.

The concentration of metal ions in the collected supernatants was determined by X-ray fluorescence spectrometry using an energy dispersive X-ray fluorescence spectrometer (Thermo Scientific, USA). The average values of duplicate analyses were reported.

The removal efficiency (%) of metal ions by the biosorbent was calculated using the following equation:

$$\textit{Removal efficiency}\ (\%) = \frac{c_i - c_f}{c_i} \cdot 100$$

where: *ci* and *cf* are the concentrations of the metal ions (mg L-1) in the initial and final solutions, respectively.

3. Results and discussion

3.1. Batch biosorption experiments

Figure 1 (a, b) shows the heavy metal ions concentrations in the acidic mine drainage after different contact times with chemical pre-treated Cyprinus carpio scales, while the values of the removal efficiency are illustrated in Figure 1 (c, d).

As expected, the removal efficiency of Mn and Zn ions gradually increases as the contact time increase regardless the chemical pre-treatment applied. By studying the influence of chemical pre-treatments applied to fish scales on the removal efficiency of Zn, the outcomes presented in Figure 1c show a 100 % removal efficiency when fish scales were treated with NaOH after the total investigated contact time. The pre-treatment of the fish scales with alkali agents (namely NaOH) could remove the lipids and proteins from the fish scale surface that disguise the reactive sites that are necessary for metal adsorption [25].

However, when fish scales were pre-treated with soluble potassium salts of humic acids and NaCl, the removal efficiencies of Zn reach slightly lower values of 93.5 % and 92 %, respectively.

Thus, chemical pre-treatment of fish scales with alkali investigated agents (NaOH and soluble potassium salts of humic acids) and NaCl has a minor effect of the removal efficiency of Zn from AMD. But as far as concern the Mn ions, the chemical

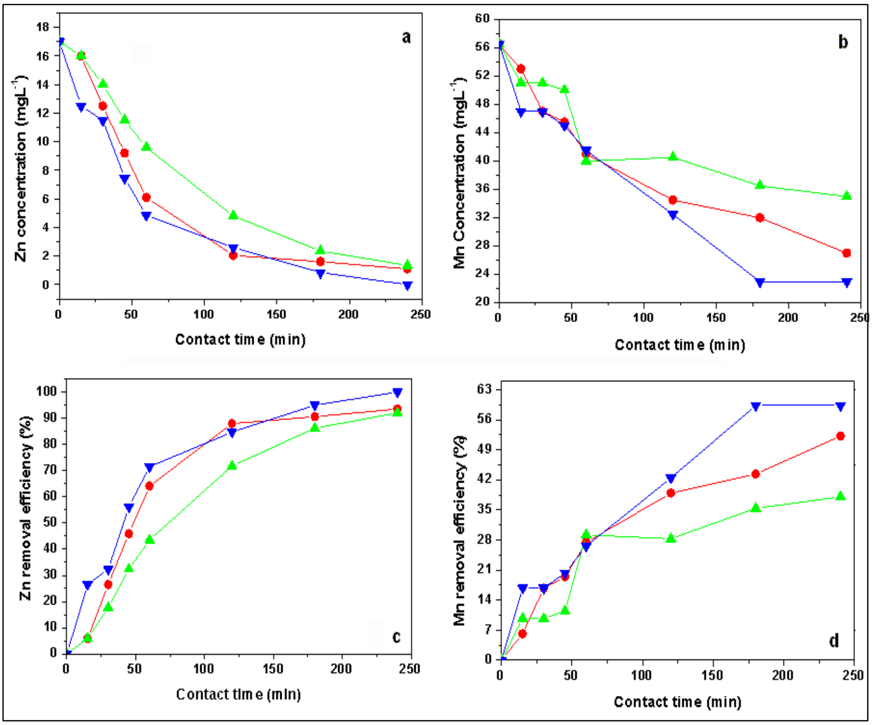

Fig. 1. Influence of the chemical pre-treatment of Cyprinus carpio scales on the concentration of Zn (a) and Mn (b) ions in AMD solution, and on the heavy metal removal efficiency (c, d) during the investigated contact time. Fish scale pre-treatments: (M) 2% soluble potassium salts of humic acids; (¶) 1M NaCl and (¶) 0.1M NaOH.

pre-treatment of fish scales with NaOH improved the removal efficiency by more than 15%, after 180 minutes of contact.

It should be pointed out that a solid:liquid ratio of 1:50 (g:mL) was sufficient to reduce the Zn concentration below the maximum consent value established by Romanian legislation, after 240 min of stirring. Instead, in the case of Mn ions, the values established by legislation were not reached.

As regards the Fe ions, the removal efficiency increases considerably during the first 15 minutes of contact (data not shown) because the solution pH also increased quickly from 1.8 to 3.5, which allowed the chemical precipitation of iron, under the form of Fe(OH)3.

In an attempt to enhance the metal removal from the AMD solution, the NaOH pre-treated fish scales were grinded and sieved in order to obtain a fine powder with the particle size of less than 1 µm. Thus, the effect of the particle sizes on the heavy metals removal efficiency was further studied for NaOH pre-treated Cyprinus carpio scales and the obtained results are presented in Figure 2.

Bringing the NaOH pre-treated fish scales to the powder stage results in an increase in Zn and Mn removal efficiency. Thus, the Zn removal efficiency increased with more than 62.6% after 30 minutes of contact when powdered NaOH pre-treated Cyprinus carpio scales were used instead of NaOH pre-treated Cyprinus carpio scales with 5-7 mm particle sizes.

In the case of Mn ions, the removal efficiency increases during the contact time with values between 21.24% to 49.55% when powdered NaOH pre-treated Cyprinus carpio scales were used.

As compared to the coarse fish scales (5-7 mm), when using the powdered NaOH pre-treated Cyprinus carpio scales, the decreases of the Fe and Zn ions concentrations below the maximum consent values was attained after 120 minutes. As regards the Mn ions, the concentration value decreased to 5.3 mg L-1 after 180 minutes of contact, with only 4.3 mg L-1 higher than the maximum consent limit.

The results obtained during the biosorption experiments indicate that powdered NaOH pre-treated Cyprinus carpio scales have good potential to remove Fe, Mn and Zn ions from the acidic mine drainage generated at "Ro ia Montana" gold mine.

3.2. SEM-EDX analysis

The results of SEM-EDX analysis performed on the NaOH pre-treated Cyprinus carpio fish scales before and after their contact with AMD are presented in Figure 3.

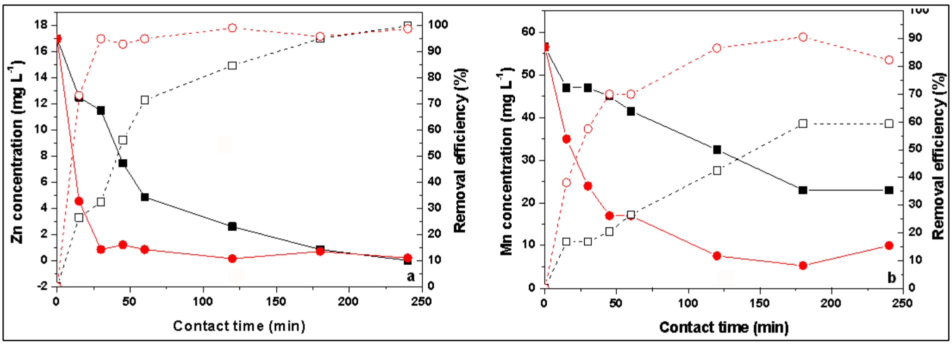

Fig. 2. Influence of the particle sizes of NaOH pre-treated Cyprinus carpio scales on the removal efficiency of Zn and Mn ions from AMD solution during the investigated contact time (a, b). Fish scale particle size: (#) 5-7 mm; (M) powder.
(! !) Concentration data. (- - - -) Removal efficiency data.

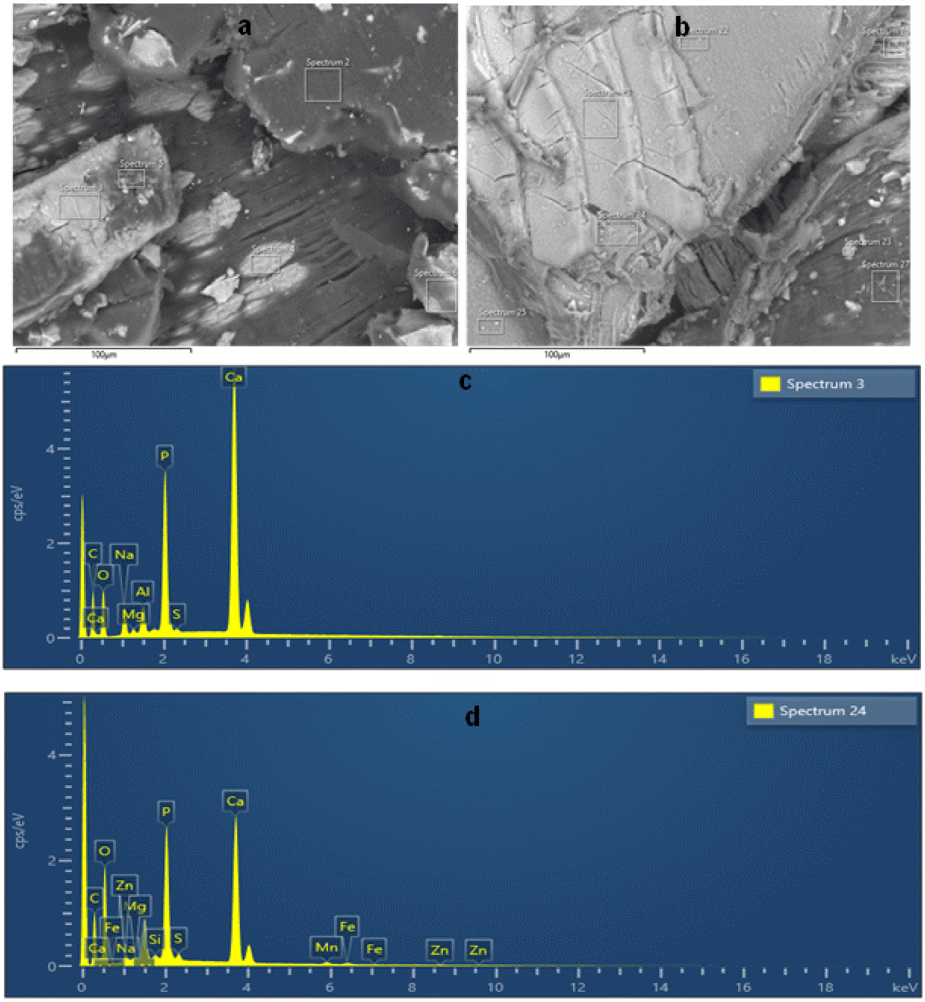

Fig. 3. SEM image of NaOH pre-treated powder fish scales before (a) and after (b) the contact with AMD solution. EDX spectra of NaOH pre-treated powder fish scales before (c) and after (d) the contact with AMD solution.

The presence of the Fe, Mn and Zn traces on the surface of the NaOH pre-treated in the EDS spectrum of the chemically treated fish scales confirms their ability to remove these pollutants from the acidic mine drainage generated at “Ro ia Montana” gold mine.

4. Conclusions

In the present study, the chemically pre-treated Cyprinus carpio scales have been proved as effective biosorbents for Fe, Mn and Zn ions from real AMD. The efficacy of chemical pre-treatment agents follows the next order: NaCl < soluble potassium salts of humic acids < NaOH. A solid:liquid ratio of 1:50 (g:mL) was sufficient to remove 100 %, 82.3 % and 98.08 % of iron, manganese, and zinc from AMD solution after 240 min of contact with the finest-grained NaOH pre-treated Cyprinus carpio scales.

The adsorptive properties of NaOH pre-treated Cyprinus carpio scales were also proved by the results of SEM-EDX analysis which revealed the occurrence of the three metals on the surface of the sorbent.

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