Assessment of *Cyprinus carpio* Scales as a Low-Cost and Effective Biosorbent for the Removal of Heavy Metals from the Acidic Mine Drainage Generated at Rosia Montana Gold Mine (Romania)

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Abstract: In the present study, the biosorptive potential of *Cyprinus carpio* scales for the removal of Fe, Mn, and Zn ions from real acidic mine drainage (AMD) generated at the Rosia Montana gold mine (Romania) was explored for the first time. The collected AMD solution is very acidic, and the concentrations of Fe, Mn, and Zn ions exceed more than 34 to 56 times the disposal standards imposed by legislation. Batch adsorption experiments were carried out to study the effect of the sorbent dosage, sorbent particle size, pH, and contact time on the adsorption performance of the fish scales. Before and after the adsorption process, the biosorbent was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy, and energy-dispersive X-ray spectroscopy (SEM-EDX). In the investigated experimental conditions, about 100%, 87.1%, and 100% of Fe, Mn, and Zn ions were removed from the AMD after 240 min of contact with the finest-grained *Cyprinus carpio* scale samples using a solid:liquid ratio of 20:1 (g:L). The adsorption data were analyzed using the pseudo-first order, pseudo-second order, intraparticle diffusion rate, and Elovich equations. The adsorption process was found to follow the pseudo-second-order kinetic model. The maximum adsorption capacities of the fish scales were about 2.46 mg/g for Mn and 0.85 mg/g for Zn ions, respectively. Aside from their significant efficiency in the removal of metals from AMD, *Cyprinus carpio* scales also have the potential to neutralize the acidic wastewater. Thus, the removal process of metal ions from AMD is ruled by a complex mechanism, including adsorption and iron precipitation. The recycled scales are still able to remove the metal ions from AMD with a better performance during the first regeneration cycle. Based on the obtained results, it might be assessed that the low-cost biowaste of *Cyprinus carpio* scales have great potential and could be effectively used for the remediation of real acidic mine drainage from a sustainable perspective.

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

1. Introduction

Industrialization activities have brought many disturbing changes in the environment due to the disposal and discharge of huge amounts of solid and liquid wastes. For example, more than 50% of the remaining material from fish processing plants and large culinary establishments is not used as food and produces almost 32 million tons of waste [1], creating huge economic and environmental concerns [2]. Fish processing industries generate large quantities of fish scales as processing waste. Fish scales are hard to degrade, causing difficulty in waste management and environmental pollution if not treated.

Likewise, acidic mine drainage (AMD) is an inevitable byproduct of the mining production of sulfide minerals [3]. AMD originates from both active and abandoned mines (primarily gold and coal) [4]; it is highly acidic and contains elevated concentrations of toxic substances, mainly heavy metal ions (i.e., Fe, Zn, Mn, Cu, Pb, Cr, Ni, and Cd) that cause long-term pollution problems [3,5] by damaging the ecosystems of soil and receiving rivers or lakes and corroding the infrastructure [6]. These hazardous pollutants can be
further transferred to humans through various exposure pathways and potentially have teratogenic, carcinogenic, and mutagenic effects on living organisms upon exposure [4,7]. In this context, the removal of heavy metals from acidic mine drainage has become one of the most imminent problems for environmental experts.

Conventional technologies used for the treatment of AMD, such as active (driven by frequent input of chemicals, energy, and equipment) and passive (based on oxidation or reduction) methods cannot effectively address the problem of environmental pollution, mainly due to their reduced performance, high cost, and the generation of toxic and hazardous waste (sludge and/or brines) that could produce secondary pollution [4]. Other techniques, such as precipitation [8], electrocoagulation [9], constructed wetlands [10], and adsorption [11] have also been proposed as alternative treatments for AMD remediation. Among these methods, adsorption presents several advantages, such as high reliability and efficiency, design simplicity, ease of operation, and recyclability [12]. Several recent reviews [13–15] revealed that various materials, including zeolites, activated carbon, fly ash, clay/earth-based materials as well as different composites [16–21] and nanomaterials [22], could be used as effective adsorbents for the removal of heavy metals from wastewater.

In recent years, the global scientific community has been focused on the use of biomaterials, which are byproducts or waste from the agriculture and large-scale food industries. Reducing the ability to constitute a nuisance when they are discarded into the environment, various biomaterials have been investigated as efficient, low-cost, easily available adsorbents for the removal of various pollutants (heavy metals, dye, anions, etc.) from wastewater [23–27]. Among them are animal bones, fish waste (bones, scales, etc.), crab shells, arca shells, algal and seaweed biomass, eggshells, rice husks, nut shells, potato peels, starch, sawdust, fruits peels, sugar cane bagasse, etc. [5,28–34], which show levels of heavy metals uptake high enough to justify further research. Additionally, by using biowaste as adsorbent materials, a sustainable and circular economy can be achieved [35].

Regarding the fish wastes, scales are waste material with no important competitive use. Fish wastes are partially used to produce fertilizers and fish oil with low profitability or as raw material for direct feeding in aquaculture [36–39] and partly thrown away [40]. To overcome the environmental issues and for the full use of biomass for the purposes of high-commercial value, fish wastes were also investigated as a potential resource to produce value-adding products (i.e., proteins, peptides, collagen, enzymes, and oils) [40]. Recently, fish wastes have acquired special attention as a potential source of chitin and derivatives, with a particular focus on fish scales [2].

Fish scales consist mainly of closely packed 70 to 80 nm diameter type I collagen fibers [41] surrounded by hydroxyapatite and other calcium compounds that might possess certain adsorptive properties [42]. Recent studies have reported the potential of several fish scale types to behave as low-cost and eco-friendly biosorbents for the removal of heavy metals and dyes [42–47] from solutions. A summary of the performance of various fish scale types in the removal process of heavy metal ions from synthetic solutions is presented in Table 1.

Table 1. Performance of several fish scale types in the removal process of heavy metal ions from synthetic solutions *

| Fish Species         | Heavy Metal | Conc. (mg L⁻¹) | Optimum Parameters for Biosorption (Dosage, pH, Contact Time) | q_max (mg g⁻¹) | R.E. max (%) | Ref. |
|----------------------|-------------|----------------|---------------------------------------------------------------|----------------|--------------|------|
| *Micropogonias undulatus* | Zn          | 1000           | 7.01 g/L; pH 5.4; 2.5 h                                        | 159.4          | 96.45        | [48] |
Table 1. Cont.

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|--------------|-------------|----------------------|---------------------------------------------------------------|-----------------------------|------------------------|-----|
| Oreochromis niloticus | Fe | 0.3 | 0.8 g/100 mL; pH 4.5; 3 h | 0.02407 | 64.2 | [49] |
| | Zn | 0.01 | 0.02 g/100 mL; pH 6; 3 h | 0.04569 | 92.3 | |
| | Zn | 60 | 1 g/L; pH 3.0; 24 h | 13 | - | [44] |
| | Fe | 400 | Zn | 60 | 20 g/L; pH 1; 24 h | - | 67 | [50] |
| | Pb ** | 30 | Cu | 175 | 1 g/50 mL; pH 3.0; 12 h | 20.6 | 95 | [51] |
| Dicentrarchus labrax | Cu | 200 | 1 g/L; pH 3.0 | 77.4 | - | [52] |
| Tilapia mossambica | Fe | 0.3 | 0.8 g/100 mL; pH 4.5; 3 h | 0.0152 | 65.9 | [53] |
| | Zn | 0.01 | 0.02 g/100 mL; pH 6; 3 h | 0.04676 | 93.52 | |
| Fish scale | Cr(III) | 150 | 0.8 g/100 mL; pH 5.0; 15 h | 18.7 | 99.75 | [54] |
| Lates niloticus sp. | Cr(VI) *** | 0.158 | 0.5 g/100 mL; pH 2.0; 3.3 h | 27.270 | 50.63 | [55] |
| Sardina pilchardus | Cd | 75 | 0.25 g/L; pH 3.0; 1 h | 12.94 | 88.2 | [56] |
| Mixed fish scale | Zn | 100 | 76.99 mg/50 mL, pH = 7.52; 1 h | - | 81.97 | [57] |
| | Pb | 100 ** | Mn | 50 | 5 mg/50 mL; pH = 7; 5 h | - | 90.0 | [58] |

Notes: * Single component solutions, except if something else is specified. ** Multicomponent synthetic solution based on the properties of a real effluent from automotive recycling industry. *** Wastewater from tannery industry.

The literature survey revealed that most of the reported studies used synthetic solutions in which one or few metal ions are present [59,60]. While the evaluation of the performance of fish scales as biosorbents of heavy metal ions from real wastewater is very scarce [57,58], this is probably due to the complex composition of these solutions, which greatly complicates the removal processes.

In light of the above-highlighted drawback, the present work aims to explore the effectiveness of local fish scale (*Cyprinus carpio*) waste as a new biosorptive approach in the removal of three targeted heavy metals ions (Fe, Mn, and Zn) from real acidic mine drainage generated at the “Roșia Montană” gold mine in Romania. The influence of several parameters such as biosorbent dosage, biosorbent particle size, pH, and contact time on the removal efficiency of the metals from the acidic mine drainage was studied using the batch technique. The interactions between the metal ions and the fish scales were explored by FTIR and SEM-EDS analysis. To understand the adsorption mechanism of the metal ions on the fish scales, four kinetics models were examined. Some experiments exploring the regeneration and reusability of the biosorbent were also carried out. The proposed removal method is based on selectivity, sensitivity, and cost-effectiveness as compared to other similar studies [17,61,62].

2. Materials and Methods

2.1. Acidic Mine Drainage Sample

An actual acidic mine drainage (AMD) sample collected from “Roșia Montană” gold mine (GPS coordinates: 46°18’09.1” N, 23°07’04.4” E) from Romania was used for the biosorption experiments. “Roșia Montană” gold mine is located in the Apuseni Mountains in the west of Romania, Alba County (Figure 1). The history of gold mining in this region dates back to the times of the Roman Empire [63].
In the eighteenth and nineteenth centuries, extensive mining was performed and a network of underground mines covering hundreds of kilometers was developed. Historically, mining activities performed at “Roșia Montană” have led to extensive problems in the ecosystem surrounding the area [64]. Processing and extraction of ores rich in metals such as gold and silver and the disposal of mine tailings are the mining operations that mostly caused contamination of the environment with metalloids and heavy metals, particularly the contamination of water, soil, and vegetation around the “Roșia Montană” gold mining area [65].

The acidic mine drainage was collected on 20 March 2022 from a naturally formed channel in front of the mining gallery.

The pH of the raw AMD was measured on-site using a portable pH meter (Hanna Instruments, Woonsocket, RI, USA). Immediately after collection, the wastewater sample was acidified to pH = 1.8 with concentrated nitric acid to avoid the precipitation of metals, then filtered and stored at 4 °C until analysis.

The chemical composition of the AMD was estimated in laboratory by X-ray fluorescence spectrometry using an ARL Quant’X spectrometer (Thermo Fisher Scientific, Waltham, MA, USA).

2.2. Biosorbent Preparation

The fish scale waste was collected from a local market and came from Cyprinus carpio in the Danube (Romania). The fish scales were soaked in water for 24 h then washed several times to remove the adhering dust and soluble impurities from their surface and finally rinsed with distilled water. Afterward, the fish scales were dried at 60 °C in an oven (UE 400 Memmert, Schwabach, Germany) until a constant weight was achieved and further used in the biosorption experiments (referred to as raw scales).

A quantity of dried scales was cut into small pieces of 5–7 mm (referred to as fine scales), and another quantity was converted into a fine powder using a laboratory grinder (GM 200, Retsch, Haan, Germany). The obtained powder was first sieved through an octagon sieve, and the fraction less than 800 µm in size was collected for further use.

2.3. Batch Adsorption Experiments and Metal Analysis

The experiments were carried out in batch mode to analyze the removal capabilities of the fish scales at room temperature (25 °C). The adsorption studies were conducted at
a constant agitation speed (500 rpm). A fixed volume of acidic drainage water collected from “Rosia Montana” gold mine (100 mL) was put in contact with a predefined mass of fish scales for 240 min. The mass of the biosorbent varied from 0.5 g to 2 g. During the first hour in which the fish scales were in contact with the AMD solution, under continuous stirring, supernatants were extracted at 15 min intervals using a micropipette. Then the supernatants were collected every 60 min for the next 4 h. The separation of the sorbent and solutions was carried out by filtration process using filter papers. During the experiments, the pH changes were continuously monitored using a glass electrode and a pH meter (Hanna Instruments).

The residual concentration of metal ions (Fe, Mn, and Zn) in the collected supernatants was immediately determined by X-ray fluorescence spectrometry using a Quant’X ARL energy-dispersive X-ray fluorescence spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) which provides detection limits at the sub-ppm level.

The removal efficiency of the metal ions (R.E.) by the adsorbent was estimated using Equation (1). The metal adsorption capacity of the fish scales $q_e$ was calculated from the mass balance with Equation (2).

$$\text{R.E.} \, (\%) = \left[\frac{(C_i - C_e)}{C_i}\right] \times 100,$$

$$q_e \, (\text{mg g}^{-1}) = \left[\frac{(C_i - C_e) \times V}{M}\right],$$

where $C_i$ and $C_e$ are the concentrations of the metal ions (mg L$^{-1}$) in the initial and final solutions, respectively; $V$ is the sample volume (L); and $M$ is the adsorbent mass (g).

All the experiments and analyses were performed in duplicate, and the average values were reported.

2.4. Desorption Experiments

To investigate the possibility of repeated use of the metals-loaded fish scales, desorption experiments were conducted using two different reagents, namely HCl and NaCl. For this purpose, 3 g of metals-loaded fish scales were treated under continuous stirring for 24 h with 300 mL solution of HCl 0.1 N or NaCl 1 N, respectively. The recycled fish scales were extensively washed with distilled water until a neutral pH was achieved, then filtered, and dried at 35°C for the next 4 h. Two cycles of desorption–adsorption were performed to examine the fish scales’ reusability.

2.5. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR absorption spectra of the fish scales before and after contact with AMD solution were recorded in KBr pellet using a Bruker Vector 22 FT–IR spectrometer from 4000 to 400 cm$^{-1}$.

2.6. Scanning Electron Microscopy-Energy-Dispersive X-ray Spectroscopy (SEM-EDX)

The morphological characteristics of the fish scales before and after contact with AMD solution were determined by scanning electron microscopy (SEM) using a tungsten filament at 20 kV acceleration voltage and a working distance of about 10 mm. The elemental chemical analysis of the samples was performed using an energy-dispersive X-ray spectrometer (EDX). A TM4000plus II scanning electron microscope (Hitachi, Tokyo, Japan) coupled with a liquid-nitrogen-free EDS mapping detector (Oxford Instruments, Oxford, UK) was used for this purpose.

3. Results and Discussion

3.1. Characterization of AMD Collected from the “Rosia Montana” Gold Mine

The water drainage collected from the “Rosia Montana” gold mine was highly acidic (pH = 2.8), and the heavy metal concentrations were significant. Table 2 shows the average chemical composition of the AMD samples collected from the “Roșia Montana” gold mine.
Table 2. Chemical composition of the AMD sample collected from “Rosia Montana” gold mine.

| Element | Unit   | Value | Maximum Consent Limits *
|---------|--------|-------|----------------------------|
| Fe      | mg L$^{-1}$ | 201.5 | 5.0                         |
| Mn      | mg L$^{-1}$ | 56.5  | 1.0                         |
| Zn      | mg L$^{-1}$ | 17    | 0.5                         |

Note: * According to NTPA 001/2002 (Romanian legislation).

The concentrations of Zn, Fe, and Mn ions in the acidic mine drainage collected from the “Rosia Montana” gold mine exceeded more than 34 to 56 times the maximum consent limits established by Romanian regulatory standard [66]. Copper, cadmium, and nickel were also identified in the acidic mine drainage but in low concentrations. As illustrated in Figure 2, the acidic mine drainage is disposed into the environment without any remediation treatment and threatens the functioning of the nearby ecosystem.

![Water drainage at “Rosia Montana” gold mine gallery.](image)

Thus, it is evident that it is compulsory to collect and treat this acidic mine drainage water.

3.2. Batch Adsorption Experiments

It is known that during the adsorption studies, the initial adsorbate concentration, adsorbent dosage, particle size, and contact time with the adsorbate from the contaminated solution are the important parameters governing the extent of the adsorption. Likewise, the initial pH of the solution and its variation during the contact time with the adsorbent is another crucial factor that controls the adsorption process, influencing the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate into the solution [67,68].

Therefore, in this section, the effect of different experimental variables, such as the fish scale particle size, fish scale dosage, and contact time, which are conventionally used to optimize the experimental conditions for the maximum metal ions uptake by the proposed biosorbent, is described comprehensively.

Figure 3 shows the residual concentrations of Fe, Mn, and Zn ions in the acidic mine drainage after different contact times with various dosages of *Cyprinus carpio* scales and the corresponding values of the metals’ removal efficiency. The variation of the solution pH during contact with three doses of the biosorbent is also presented in Figure 3.

As expected, a depletion in the concentration of the metal ions in the AMD solution took place during the contact period with the *Cyprinus carpio* scales regardless of their dosages. However, this decreasing trend in the metal ions concentration over time was rather low, especially in the case of the Zn and Mn ions when the lowest dosage of fish scales was used. By increasing the amount of fish scales added to the AMD solution, there was a rapid decrease in the Fe and Zn ions concentrations, which reached the equilibrium
condition within the first 15 and 60 min, respectively. Instead, the Mn ions concentrations decreased slower over the contact time with the fish scales and gradually reached the equilibrium condition after about 200 min.

It is worth mentioning that the residual concentration of Zn ions in the AMD solution attained a value below 0.5 mg L\(^{-1}\), which is the threshold limit imposed by Romanian legislation [66], after 30 min of contact with the highest tested amount of fish scales (2 g). Instead, in the case of Mn ions, the lowest residual concentration value of 7.25 mg L\(^{-1}\) was attained after 240 min of contact with 2 g of fish scales. This value exceeds the maximum consent limit (1 mg L\(^{-1}\)), which means that additional treatment steps are necessary to meet the imposed regulation limit.

The rapid and significant decrease of Fe ions concentration within the first 15 min of contact between the AMD and fish scales (Figure 3a) could be explained by the variation of the solution pH over the contact time. As depicted in Figure 3d, the fish scales have the ability to quickly increase the pH of the acidic mine drainage as their dosage increases. As previously reported [44], this behavior might be due to the alkaline character of fish scales, which suffer a leaching process in their mineral phase (apatite) when in contact with strong acidic wastewater, releasing various species (i.e., phosphate, Ca\(^{2+}\) ions, etc.) into the solution during the biosorption process and thus making the medium more alkaline. This allowed the removal of Fe ions from the AMD through precipitation when the value of the solution pH exceeded 3.5. This hypothesis was confirmed by the results of the chemical analysis which also revealed an increase of the Ca ions concentration in the AMD solution during contact time with the fish scales. It should also be mentioned that a change in the liquid-phase color from yellow to orange-reddish was observed during the batch experiments within the first 15 min of contact between the fish scales (1 g and 2 g) and AMD, and it likely comes from the precipitation of iron as Fe(OH)\(_3\). As expected, the calculated removal efficiency of Fe ions from AMD attains 90.6% and 100% in the presence of fish scales at dosages of 0.5 g and 2 g, respectively.

In this context, the data regarding iron removal from AMD will not be further discussed. Nevertheless, the important neutralization potential of Cyprinus carpio scales should be highlighted since it might allow the treatment of acidic effluents, including the precipitation of iron in a sustainable and cost-effective way.

Regarding the removal efficiency values for Zn and Mn ions, a positive correlation with the fish scale dosage could be noticed in Figure 3b,c, possibly due to greater availability of exchangeable sites or surface area at a higher concentration of sorbent [49]. For instance, in the case of Zn ions, the R.E. values increased significantly from 11.76% to 97.35% after 30 min of contact when the scale dosage was increased from 0.5 to 2 g. Likewise, a significant augmentation of the manganese removal percentages from 16.81% to 38.05% and then to 87.16% was noticed after 240 min of contact with 0.5, 1, and 2 g of fish scales, respectively. The removal process of Zn and Mn ions could be attributed to their adsorption onto the fish scales since the pH values for the hydroxides precipitation were not reached.

The effect of particle size on the heavy metals removal efficiency was further studied for the most efficient investigated dosage of Cyprinus carpio scales, and the obtained results are presented in Figure 4.
Instead, in the case of Mn ions, the lowest residual concentration value of 7.25 mg L\(^{-1}\) was attained after 240 min of contact with 2 g of fish scales. This value exceeds the maximum consent limit (1 mg L\(^{-1}\)), which means that additional treatment steps are necessary to meet the imposed regulation limit.

**Figure 3.** Cont.
Figure 3. Influence of Cyprinus carpio scale dosage on the residual concentrations of metal ions in AMD solution (a–c) and the calculated removal efficiency values (a′–c′) after various contact times. Variation of the pH of AMD solution during the contact time with various dosages of fish scales (d). Fish scale dosage: (■) 0.5 g; (●) 1 g and (▲) 2 g.

Figure 4. Influence of the Cyprinus carpio scale grain sizes on the residual concentrations and removal efficiency of Mn (a) and Zn (b) ions from AMD solution after various contact times. Fish scale grain size: (■, □) raw (as received); (●, ○) fine; and (▲, △) powder. (---) Residual concentration data. (- - - -) Removal efficiency data.

As shown in Figure 4, the R.E. values were low immediately after the AMD contacted the raw fish scales, attaining 5% for Zn and 7% for Mn ions, respectively. A progressive increase of R.E. values could be noticed as the contact time elapsed, and after 240 min, about 95.6% of Zn ions and 46.9% of Mn ions were removed from the AMD solution. The addition of the fine-grained-sized Cyprinus carpio scales (5–7 mm) did not markedly improve the removal percentages of the Zn and Mn ions from the AMD as compared to the raw ones (Figure 4). Instead, the removal performances of the powder scales increased sharply within the first 15 min of contact with the AMD solution and reached 91.17% for Zn ions and 52.2% for Mn ions, respectively. This behavior is probably due to the availability of a large surface area on the powder scales [42,54] and the initially high differences in the concentrations of the bulk solution and solid-liquid interface [69]. Furthermore, the increase in the solution pH value to 5.2 with the addition of the powder fish scales might...
have led to a deprotonation of the bisorbent surface, which could increase the negatively charged sites and further enhance the attraction forces between the scales’ surface and the metal ions, leading to an increase in the adsorption capacity [70].

Nonetheless, upon increasing the contact time, the performance of the powder scales for Zn ions removal increased slightly and attained equilibrium after about 60 min when the calculated R.E values were around 99%. In order to explain this behavior, it was assumed that the active sites of the fish scales were exhausted once the equilibrium had been achieved, and the rate of uptake was further controlled by the rate at which the metal was transported from the exterior to the interior sites of the sorbent particles [71]. Thus, the removal process of Zn ions occurred in two phases, very fast adsorption followed by slow diffusion. Similar conclusions were formerly obtained by other researchers [35,53,72].

The results obtained during the batch adsorption studies indicate that *Cyprinus carpio* scales have a great potential to remove the metallic ions from the acidic mine drainage generated at the “Rosia Montana” gold mine through a complex mechanism, involving mainly the adsorption process along with the concomitant precipitation of the Fe ions. Moreover, a possible ion exchange between the calcium ions and the metallic cations from the AMD solution could also take place. Similar results were reported by Ribeiro et al. [50], which showed that *Oreochromis niloticus* fish scales have a great neutralization potential for extremely acidic solutions (pH = 1), and the removal process of heavy metals involves adsorption and other complex simultaneous phenomena, such as ion exchange, precipitation, and/or complexation.

3.3. SEM-EDX Analysis

In an attempt to investigate the morphological properties of the *Cyprinus carpio* fish scales and to estimate their chemical composition, SEM and EDX analyses were performed before and after contact with the acidic mine drainage.

SEM micrograph and EDX spectra of the raw fish scales are presented in Figure 5. Table 3 shows the elemental composition of the fish scales before and after the heavy metals removal processes.

As depicted in Figure 5a, the powdered fish scales appear to have a relatively smooth surface characterized by the presence of dark and light (white) regions. The results of EDX analysis (Figure 5c and Table 3) show that the white region is rich in inorganic material containing calcium (15.37 at.%), phosphorus (5.48 at.%), and carbon (58.46 at.%), probably corresponding to the carbonated apatite \( \text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3 \) and hydroxyapatite \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \) [44] considering that the calcium to phosphorus (Ca/P) ratio exceeds 1.67, which is the reported value of Ca/P ratio in hydroxyapatite [73,74].

The darker region is mainly composed of organic material, i.e., proteins (most likely type I collagen), containing large amounts of carbon (51.89 at.%), oxygen (26.16 at.%), and nitrogen (16.10 at.%). In addition, small amounts of Mg and S were also detected. The presence of the Mg traces in the fish scales was previously reported in the case of *Oreochromis niloticus* scales, and it was associated with the functional groups in the organic phase and disperse in the inorganic matrix (i.e., substituted in the structures of apatite) [44].

Figure 6 shows the surface morphology of two scale samples that have been in contact with the AMD solution for 240 min and the corresponding EDX spectra.

As illustrated in Figure 6, the morphology of the fish scales does not significantly change after contact with the AMD solution. Instead, the EDX spectra from Figure 6 reveal the presence of the Fe, Mn, and Zn peaks which were not previously detected in the raw scales (Figure 5). These results confirm the ability of *Cyprinus carpio* scales to retain heavy metals from AMD solution.
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In an attempt to investigate the morphological properties of the Cyprinus carpio fish scales and to estimate their chemical composition, SEM and EDX analyses were performed before and after contact with the acidic mine drainage.

Figure 5. SEM micrograph of the powder Cyprinus carpio scales 500× (a); EDX spectra corresponding to the two regions identified on the surface of the scales: (b) darker-spectrum 1 and (c) whiter-spectrum 2.

Table 3. EDX analysis of the Cyprinus carpio scales before and after 240 min of contact with the acidic mine drainage solution.

| Element | Before Contact with AMD | After Contact with AMD |
|---------|------------------------|------------------------|
|         | Darker Region (Spectrum 1) | Whiter Region (Spectrum 2) | Whiter Region (Spectrum 3) | Darker Region (Spectrum 2) |
| C       | 51.89 at.%             | 58.46 at.%             | 63.80 at.%             | 40.83 at.%             |
| O       | 26.16 at.%             | 20.35 at.%             | 28.02 at.%             | 40.66 at.%             |
| Ca      | 3.21 at.%              | 15.37 at.%             | 2.45 at.%              | 4.80 at.%              |
| P       | 2.38 at.%              | 5.48 at.%              | 1.87 at.%              | 3.74 at.%              |
| N       | 16.10 at.%             | -                    | -                    | 9.48 at.%              |
| Mg      | 0.20 at.%              | 0.26 at.%              | 0.24 at.%             | 0.15 at.%              |
| S       | 0.06 at.%              | 0.08 at.%              | 0.21 at.%             | 0.15 at.%              |
| Si      | -                     | -                    | 0.10 at.%             | -                     |
| Fe      | -                     | -                    | 1.14 at.%             | 0.04 at.%              |
| Mn      | -                     | -                    | 0.07 at.%             | 0.15 at.%              |
| Zn      | -                     | -                    | 0.07 at.%             | 0.05 at.%              |
| Ca/P    | 1.35                   | 2.80                  | 1.31                  | 1.28                  |
| C/O     | 1.90                   | 2.87                  | 2.35                  | 1.00                  |

As depicted in Figure 5a, the powdered fish scales appear to have a relatively smooth surface characterized by the presence of dark and light (white) regions. The results of EDX analysis (Figure 5c and Table 3) show that the white region is rich in inorganic material containing calcium (15.37 at.%), phosphorus (5.48 at.%), and carbon (58.46 at.%), probably corresponding to the carbonated apatite [Ca_{10}(PO_4)_6CO_3] and hydroxyapatite [Ca_{10}(PO_4)_6(OH)_2] considering that the calcium to phosphorus (Ca/P) ratio exceeds 1.67, which is the reported value of Ca/P ratio in hydroxyapatite [73,74].

The darker region is mainly composed of organic material, i.e., proteins (most likely type I collagen), containing large amounts of carbon (51.89 at.%), oxygen (26.16 at.%), and nitrogen (16.10 at.%). In addition, small amounts of Mg and S were also detected. The presence of the Mg traces in the fish scales was previously reported in the case of Oreochromis niloticus scales, and it was associated with the functional groups in the organic...
Table 3. EDX analysis of the *Cyprinus carpio* scales before and after 240 min of contact with the acidic mine drainage solution.

| Element | C | O | Ca | P | N | Mg | S | Fe | Mn | Zn | Ca/P | C/O |
|---------|---|---|----|---|---|----|---|----|----|----|------|-----|
| **Before Contact with AMD** | | | | | | | | | | | | |
| Darker Region (Spectrum 1) | 51.89 | 26.16 | 3.21 | 2.38 | 16.10 | 0.20 | 0.06 | - | - | - | 1.35 | 1.90 |
| Whiter Region (Spectrum 2) | 58.46 | 20.35 | 15.37 | 5.48 | 0.26 | 0.26 | 0.08 | - | - | - | 2.80 | 2.87 |
| **After Contact with AMD** | | | | | | | | | | | | |
| Darker Region (Spectrum 1) | 63.80 | 28.02 | 2.45 | 1.87 | - | - | - | - | - | - | 1.31 | 2.35 |
| Whiter Region (Spectrum 2) | 40.83 | 40.66 | 4.80 | 3.74 | 0.15 | 0.15 | 0.15 | 0.15 | 0.05 | 0.05 | 1.28 | 1.00 |
| Whiter Region (Spectrum 3) | 45.15 | 40.42 | 7.86 | 5.44 | 0.25 | 0.13 | 0.10 | 0.16 | 0.20 | 0.29 | 1.44 | 1.11 |

The high amounts of Fe identified on some parts of the scales’ surface (Figure 6a) suggest the surface precipitation of Fe(OH)$_3$, as illustrated in Table 3. However, the fish scales presented a reddish color after contact with the AMD solution, which could be related to some internal presence of the Fe species on the mineral zones in the scales’ structure.

The results of EDX analysis from Table 3 also show that Zn and Mn ions tend to concentrate in higher proportions on the regions where the inorganic phase is more abundant, and the value of the Ca/P ratio was considerably diminished from 2.80 (for the unmodified sorbent) to about 1.3–1.4 (for the metal-loaded sorbent). The important decrease of the Ca concentration in the mineral part of the fish scales after contact with the AMD solution might be ascribed to both the inorganic phase leaching and ion exchange reaction between the Ca$^{2+}$ ions from the scales and the metallic ions from the acidic mine drainage [44]. The lower content of the carbon might also be due to the leaching of the inorganic phase.

These results obtained by EDX analysis agree with those obtained by chemical analyses, which also revealed the iron precipitation, the considerable decrease of Mn and Zn ions concentrations, and the increase of Ca$^{2+}$ concentration in the solution at the end of the experiment.

However, the presence of trace amounts of Zn, Fe, and Mn ions could be also observed in the organic part of the scales (Figure 6b), probably due to their adsorptive binding on the functional groups from the proteins [75]. A leaching of the organic phase may have also occurred during the adsorption process, as suggested by the decrease of the C/O ratio for the metals-loaded sorbent as compared to the unmodified one (Table 3).

The elemental mapping of the fish scales’ surface after contact with the AMD solution from Figure 7 reveals the presence of adsorbed metallic ions on the sorbent surface. Nevertheless, it should be mentioned that the fish scale samples are heterogeneous, and the elemental composition could be different depending on the positions of the SEM images [76].
Figure 6. SEM micrograph of the powder fish scales after 240 min of contact with AMD solution (a); EDX spectra corresponding to the three regions identified on the surface of the scales: (b) whiter—spectrum 1 and (c) darker—spectrum 2.
AMD solution, recorded in the wavenumber range of 4000 to 400 cm$^{-1}$. The vibration of the CH stretch of the amide II, respectively. The adsorption band observed at 1446 cm$^{-1}$ is likely due to the bending vibration of the CH$_2$ group from proteins (collagen), while the C-N stretching vibration from amide III was detected at 1235 cm$^{-1}$. It could also be noticed in Figure 8, the presence of two absorption bands with peaks at 1025 cm$^{-1}$ assigned to the vibrations of the phosphate ions and at 872 cm$^{-1}$ corresponding to the vibrations of the carbonate ions substituted for phosphate ions in the apatite lattice [79], probably resulting in carbonatedapatite [78]. The absorption bands at 552–598 cm$^{-1}$ correspond to 4 symmetric P–O stretching vibrations of the phosphate groups [80] in the apatite lattice. The carbonate and phosphate ions are characteristic of the inorganic phase of the *Cyprinus carpio* scales’ structure, comprising carbonatedapatite and hydroxyapatite [50,78].

The inspection of the FTIR spectra of the fish scales after the contract with the AMD solution from Figure 8 reveals an important decrease in all the peaks’ intensities and several
shifts in the position of the absorption peaks. The main observed absorption bands shifting from 1633 to 1629 cm\(^{-1}\), 1530 to 1534 cm\(^{-1}\), 1446 to 1450 cm\(^{-1}\), 1334 to 1336 cm\(^{-1}\), and 1025 to 1029 cm\(^{-1}\) after the adsorption process suggests that phosphate ions from the apatite network and the functional groups from the collagen are involved as potential active sites for the retention of Zn and Mn ions from the AMD solution onto the scales’ surface.

![FTIR spectra](image)

**Figure 8.** FTIR spectra of the powder fish scales before (a) and after 240 min of contact with AMD solution (b).

### 3.5. Adsorption Kinetics Studies

Adsorption kinetics studies are essential in wastewater treatments, providing valuable insights into the reaction pathways and the mechanism of sorption [81]. The adsorption behavior is affected by various factors such as diffusion control, chemical reaction, or intraparticle diffusion. Several kinetic models can be used to explain the kinetics of heavy metal adsorption in batch systems [82], including pseudo-first order, pseudo-second order, intraparticle diffusion, and Elovich models. These kinetic models have been extensively applied to a wide variety of adsorption systems, from biomass to nanomaterials as sorbents and from pharmaceuticals and dyes to heavy metals as pollutants [83].

The pseudo-first-order kinetics proposed by Lagergren [84] can be expressed in a linear form as [81]:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t, \tag{3}
\]

where \(q_e\) and \(q_t\) denote the amounts of the adsorbed Zn\(^{2+}\) and Mn\(^{2+}\) ions on the fish scales at equilibrium and at any time, \(t\) (mg g\(^{-1}\)); \(t\) is the contact time (min) and \(k_1\) represents the pseudo-first-order rate constant (min\(^{-1}\)).

The pseudo-second-order kinetic model assumes that the rate-limiting step may be the chemical adsorption; it is usually expressed as follows [81]:

\[
t/q_t = 1/k_2 q_e^2 + t/q_e, \tag{4}
\]

where \(k_2\) is the rate constant of the pseudo-second-order adsorption model (g mg\(^{-1}\) min\(^{-1}\)).

The possibility of intraparticle diffusion influencing the adsorption process could be also explored based on the kinetic model proposed by Weber and Morris [85,86]. The intraparticle diffusion rate parameter is expressed in terms of the square root of time and sorption capacity in the following form [87]:

\[
q_t = k_3 t^{1/2} + C, \tag{5}
\]
where \( k_3 \) is the intraparticle diffusion rate constant (\( \text{mg g}^{-1} \text{ min}^{-1/2} \)) and \( C \) is a constant providing information about the thickness of the boundary layer.

The Elovich equation is useful in the chemisorption process and is suitable for systems with heterogeneous adsorbing surfaces [88]. The linear form of this equation is given by:

\[
q_t = \frac{1}{b_e} \ln(a_e b_e) + \frac{1}{b_e} \ln t
\]  

(6)

where \( a_e \) is the initial adsorption rate (\( \text{mg g}^{-1} \text{ min}^{-1} \)) and \( b_e \) is the Elovich constant (\( \text{g mg}^{-1} \)) [89].

Figure 9 displays the plots of each tested kinetic model applied for the sorption of Zn and Mn ions on the powdered fish scales. The accuracy of the fitting results by these models was assessed by comparing the regression coefficients (\( R^2 \)) for each expression [42].

The experimental sorption capacities (\( q_{\text{exp}} \)) and the predicted values (\( q_{\text{cal}}, k_1, k_2, k_3, a_e \)) from the kinetic models applied to the adsorption of Zn and Mn ions on the powdered fish scales are given in Table 4. The values of the regression coefficients are also included in Table 4.

| Kinetic Model                  | Mn\(^{2+}\) Ions Adsorption | Zn\(^{2+}\) Ions Adsorption |
|-------------------------------|------------------------------|-------------------------------|
| \( q_{\text{exp}} \) (mg g\(^{-1}\)) | 2.463                        | 0.850                         |
| Pseudo-first-order model      |                              |                               |
| \( k_1 \) (min\(^{-1}\))     | 0.012                        | 0.019                         |
| \( q_{\text{cal}} \) (mg g\(^{-1}\)) | 1.087                       | 0.982                         |
| \( R^2 \)                    | 0.9472                       | 0.7399                        |
| Pseudo-second-order model     |                              |                               |
| \( k_2 \) (g min\(^{-1}\) mg\(^{-1}\)) | 0.023                       | 0.910                         |
| \( q_{\text{cal}} \) (mg g\(^{-1}\)) | 2.584                       | 0.855                         |
| \( R^2 \)                    | 0.9970                       | 0.9999                        |
| Intraparticle diffusion       |                              | I                             |
| \( k_3 \) (mg g\(^{-1}\) min\(^{-1/2}\)) | 0.082                       | 0.022                         |
| \( C \) (mg g\(^{-1}\))     | 1.237                        | 0.696                         |
| \( R^2 \)                    | 0.9639                       | 0.9174                        |
| Elovich model                 | II                           |                               |
| \( a_e \) (mg g\(^{-1}\) min\(^{-1}\)) | 1.36                        | 2.22 \times 10^{12}         |
| \( b_e \) (g mg\(^{-1}\))   | 2.78                         | 43.48                         |
| \( R^2 \)                    | 0.9805                       | 0.7545                        |

As could be seen in Figure 9, the pseudo-second-order kinetic model best fits the experimental data corresponding to Mn and Zn ions sorption on the fish scales since the linearity of the plotting \( t/qt \) against time offers the highest correlation coefficient values for both studied heavy metal ions, namely 0.9970 for Mn and 0.9999 for Zn ions adsorption, respectively.

In addition, the calculated adsorption capacity values for the pseudo-second-order kinetic model are very close to the experimental ones (Table 4). These results suggest that the adsorption process of metals from the acidic mine drainage on Cyprinus carpio scales follows the pseudo-second kinetic model, probably involving chemical interactions between the metal ion and the surface functional groups on fish scales adsorbent. Similar results were obtained in the case of Pb biosorption by Labeo rohita scales [82], for Zn and Pb adsorption onto Micropogonias undulatus scales [48], and for Cr (III) removal by a synthesized biosorbtent from the fish scales [54].
Figure 9. Cont.
Table 5. Comparison of the maximum adsorption capacity and removal efficiency of various biosorbents used for the removal of Fe, Zn, and Mn ions from AMD solution.

| Biosorbent          | Heavy Metal | Conc. (mg L⁻¹) | Optimum Parameters for Biosorption (Dosage, pH, Contact Time) | q_max (mg g⁻¹) | R.E. max (%) | Ref.     |
|---------------------|-------------|----------------|---------------------------------------------------------------|----------------|--------------|----------|
| Peat moss           | Cu          | 116            | 20 g/100 mL, pH 2.5, 2 h                                       | -              | 87           | [90]     |
|                     | Zn *        | 108            |                                                               | -              | 61.1         |          |
| Shrimp shell waste  | Fe          | 83.24          | 11.46 g/L, pH 2.79, 24 h                                      | 17.43          | 90           | [91]     |
|                     | Zn *        | 5.94           |                                                               | 3.87           | 88           |          |
|                     | Mn *        |                |                                                               | 1.38           | 93           |          |
|                     | Fe *        | 2.12           | 2 g/L, pH 5.9, 5 h                                            | 1.1            | 88           | [93]     |
| Brewing waste       | Mn          | 0.39           |                                                               | 0.5            | 83           |          |
| Eucalyptus tereticornis | Fe          | 127            | 10 g/100 mL, pH 2.3, 3 h                                      | -              | 96           | [94]     |
|                     | Zn *        | 29             |                                                               | -              | 75           |          |
| Pig bristles        | Zn *        | 3.55           | 1 g/200 mL, pH 4.0, 1 h                                       | 0.62           | 87           | [95]     |
|                     | Mn *        | 3.32           |                                                               | 0.36           | 56           |          |
| Nut hull            | Cu          | 116            |                                                               | -              | 40           | [90]     |
|                     | Zn *        | 108            | 10 g/100 mL, pH 2.5, 2 h                                      | 10.08          | 100          | Present study |
| Cyprinus carpio scales | Fe        | 201.5          |                                                               | 10.08          | 100          | Present study |
|                     | Zn *        | 17             | 2 g/100 mL, pH 1.8, 4 h                                       | 0.850          | 100          | Present study |
|                     | Mn *        | 56.5           |                                                               | 2.463          | 87.1         | Present study |

Note: * Real AMD solution.

As shown in Table 5, the performances of Cyprinus carpio scales in the removal process of the metal ions were found comparable and competitive with those reported for other low-cost biosorbents previously used for the remediation of acidic mine wastewater. The maximum adsorption capacity of the tested fish scales is also similar to the values reported in the literature.
3.6. Desorption and Adsorbent Reusability Tests

In order to investigate the reusability of the metals-loaded fish scales, desorption experiments were performed using two chemical reagents, namely HCl 0.1 N and NaCl 1 N solutions. The recycled fish scales were further used in the metals adsorption experiments with AMD. Two cycles of desorption–adsorption experiments were carried out accordingly, and the obtained results are summarized in Table 6.

Table 6. The effect of adsorption–desorption cycle on the efficiency of the recycled fish scales to remove the metal ions from AMD.

| Cycle | HCl-Treated Scales | NaCl-Treated Scales |
|-------|-------------------|-------------------|
|       | Fe    | Zn   | Mn | Fe | Zn | Mn |
| I     | 48.4  | 8.8  | 11.5 | 66.5 | 60.6 | 11.5 |
| II    | 37.7  | 5.9  | 10.7 | 64.5 | -  | -  |

As shown in Table 6, disregarding the nature of the reagent used in the desorption process, the recycled scales are still able to remove the metal ions from the real acidic mine drainage, especially during the first regeneration cycle but with lower performances as compared to the natural adsorbent.

Although the results of the desorption–adsorption experiments were not spectacular, it might be still possible to achieve proper waste reusability by exploiting the metal-loaded *Cyprinus carpio* scales powder as bio-modifiers for asphalt binders. A previous study [96] revealed that the fish scales powder enhances the adhesion, viscoelastic properties, temperature susceptibility, and resistance to permanent deformation of the asphalt, exerting a small effect on the aging, fatigue, and cracking resistance of the asphalt.

4. Conclusions

The potential of *Cyprinus carpio* scales as readily available, cheap, and eco-friendly adsorptive material was investigated for the removal of three targeted heavy metals ions (Fe, Mn, and Zn) from the real acidic mine drainage generated at the “Rosia Montana” gold mine in Romania. The following important conclusions could be drawn:

1. *Cyprinus carpio* scales are able to remove significant concentrations of Fe, Zn, and Mn ions from AMD, and their performances depend on the dosage and particle sizes, solution pH, and contact time. A solid:liquid ratio of 20:1 (g:L) was sufficient to reduce the concentrations of Fe and Zn ions below the threshold limits imposed by legislation, and 100%, 87.1%, and 100% of Fe, Mn, and Zn ions were removed from AMD after 240 min of contact with the powder-sized scales.
2. SEM-EDX investigations confirmed the ability of *Cyprinus carpio* scales to retain heavy metals from an AMD solution.
3. FTIR analysis suggested that both phosphate ions from the apatite network and the functional groups from collagen might be involved as potential active sites for the retention of metal ions onto the scales’ surface.
4. The adsorption process of metals ions on the scales follows the pseudo-second kinetic model.
5. *Cyprinus carpio* scales present some neutralization capacity of acidic mine drainage related to the leaching of their inorganic phase, which allowed the concomitant iron precipitation.
6. In spite of the rather limited capacity of *Cyprinus carpio* scales to be repeatedly used in the adsorption process, there might be other possibilities to recycle the metals-loaded sorbent (i.e., as a bio-modifier for asphalt binders [96]), which makes it a sustainable material for real AMD remediation.

Although the promising results obtained within this preliminary work offer an ecological and cost-effective method to reduce the environmental impact of acidic mine drainage
by adding value to worthless waste, further research, including column studies, is needed to completely understand the mechanism of metals removal from real AMD and to optimize the process.

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