Using the Low-Cost Waste Materials for Heavy Metals Removal from the Mine Wastewater

Radmila Marković[1], Jasmina Stevanović[2,*], Zoran Stevanović[1], Mile Bugarin[1], Dragutin Nedeljković[2], Aleksandar Grujić[2] and Jasna Stajić-Trošić[2]

[1]*MMI, Mining and Metallurgy Institute Bor, 19210 Bor, Serbia*
[2]*ICTM, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia*

The possibility of application of low-cost and easily available materials such as cardboard or sawdust for the heavy metals removal from the acid mine water was investigated. The sawdust was obtained from oak and fir-wood. Those materials were tested on the real acid mine wastewater that contained copper, iron, zinc, nickel, and manganese in the concentrations above the maximal allowed level. The adsorption degrees of those elements were investigated. The results were shown that the iron was mechanically removed. The results of chemical analysis of effluent obtained by the use of sawdust from fir-wood indicate that the values for iron and nickel ions were lower than allowed values by the legislative direction. The highest value for copper adsorption degree of 98.31% was achieved at pH value of 7.94. Content of manganese in the effluent and at the end of process, was near the initial value. Using the sawdust obtained from oak as the adsorption material, zinc and manganese concentration in the effluent was near the start values and copper and iron content was decreased but the values were higher than allowed.

Using the cardboard, the copper adsorption degree was up to 95 mass%, iron content was under the limit value for the applied chemical detection method. The content of the manganese was not changed and the content of the zinc was decreased but the concentration was over the maximum allowed value. [doi:10.2320/matertrans.M2011191]

1. Introduction

The acid mine wastewater may contain high concentrations of hazardous materials that have significant contribution to the environmental pollution. Usual method of exploration of sulfide ore deposits is "conventional" — pyrometallurgical method that comprises by different types of shaft and flash technologies. This method is spread worldwide as it is economically feasible for large scale operations and for copper rich feeds.[1,2]

The most common treatment of the copper ore taken from the open pit or underground mining is complex treatment which enriches low grade ore before smelting. As a consequence, solid, liquid and gaseous wastes are produced. One of the strongest impact to the environment is the acid mine drainage (AMD) water. AMD water is the result of the processes in copper mines (active or closed) when natural water percolates trough dumps, causing the pollution of both waters and soil. After the excavation, sulfide minerals are exposed to the atmospheric air and AMD waters are formed as a result of the pyrite oxidation processes.

As a result, sulfuric acid, ferrous and ferric ions are produced which enchases further oxidation of the sulfide minerals and formation of AMD water. This water contains significant amounts of copper and iron and lower concentrations of other metals such as cadmium, mercury, beryllium, lead, manganese, bismuth, zinc and nickel (their concentration is in the order of magnitude of $mg\,dm^{-3}$.[3] The release of AMD water to the natural water flows, industrial and communal fields or public sewage systems must be strictly controlled. Different technological methods can be used for the water purification and metal recovery, and finding the appropriate technique is a main problem. Beside the environmental pollution, the economic interest is to recover metals from the wastewater and to recover them as a secondary raw material.

The most common process for the metal removal from the wastewater is chemical precipitation but alternatively, electrochemical and hydrometallurgical processes have been recently developed.[4–7] The adsorption of metals from the wastewater is one of the most effective in environmental and economical manner. Various materials could be used for the adsorption. Those materials could be divided in two groups: proprietary materials (iron hydroxide coated sand, organic polymers, alumina)[8,9] or waste materials from the other processes (fly ash, red mud, biomaterials).[10–13] The usual adsorbent for the removal of the metals from water is active carbon, but it is unsuitable for the adsorption on an industrial scale, due to its high price. Alternative, low-cost adsorbents are from available wastes and side products of industrial processes.[14] The adsorbent is classified as a low-cost if it may be found in a nature or it is a side-product of an industrial process.[15] It is supposed that the mechanism of adsorption is by the model of active sites existing in the cellulose structure of sawdust and an ion exchange mechanism of adsorption.[16] These active sites contain compounds with phenol groups in their molecules are able to replace protons.

The possibility of application of cardboard and sawdust was investigated in the laboratory conditions. The sawdust was obtained from the oak and fir-wood. Real mine waste water was used for the experiments. Good results for the removal of iron were obtained with all of the examined materials, while the results for copper removal from wastewater were the same. The results for nickel and zinc were also satisfactory for different adsorption materials but the manganese concentration in the effluent was the same as initial value.

*Corresponding author, E-mail: jaca@tmf.bg.ac.rs

2. Experimental

2.1 Experimental procedure

The experiments of heavy metals removal by adsorption were done on the samples of original waste water with oak tree and fir-wood sawdust and cardboard as adsorbents. The adsorption columns were polypropylene tubes, diameter 44 mm, with hole and valve on the bottom side. The volume of the solution that passed through the column was measured by the graduated vessel that was positioned under the column. 300 cm³ of waste water was transferred trough the column that contained 20 g of adsorption material. After infusing the entire volume, the solution is blown off from the column.

The time of the experiment was measured from the moment when all of the waste water was introduced in column. The elution volume at the bottom side of the column and pH were measured. In one serial of the experiments 2 cm thick layer of the quartz sand was positioned on the top and at the bottom of the column. In other experiments, adsorption material was mixed with the quartz sand in order to improve its properties. Adsorption material was used as received, without any physical or chemical treatment prior to the experiment.[17]

The concentrations of various heavy metals were determined by the atomic emission spectrophotometer apparatus (FAAS Perkin Elmer 403), and pH value was measured on pH meter PORTABLE (pHM80).

The dimension analysis was performed by standard sieving method, on TYLER sieves. This equipment and method are in accordance with the method for determination of metal powder dimension analysis, approved by the Metal Powder Industries Federation. The apparent density was measured according to the local standard Eb11: 2007 approved by the Standard Organization.

3. Results and Discussion

3.1 Chemical characterization of materials

The waste mine water was used for the experiment without previous treatment, and the task was to remove iron. The amount of hazardous substances in sample was determined by the chemical characterization. On a basis of field measurements under different weather conditions, the amount of waste water emitted to the local water ways was estimated to 3800 m³/day. Sample of 10 dm³ of mine water, was analyzed, and the results of the chemical characterization are presented in Table 1.

From the Table 1, it is obvious that concentration of copper, iron, zinc, nickel and manganese are above the permitted value for the III/IV class of water. The concentration of cadmium is below the maximal allowed level, while the concentrations of arsenic, lead, chrome and aluminum are not defined by the regulation. Apparent density and sieve analysis of quartz sand are compiled in Table 2. Analyzing values presented in Table 2, it is obvious that content of coarse fractions (+0.425 mm) is the highest.

Results of the chemical analysis of quartz sand are presented in Table 3. From values in Table 3, it could be seen that silicon is major component, and that the values of

Table 1 Chemical characterization of mine water.

Characteristics	Unit	Mine water	Legislatively
Temperature of water/air	°C	—	<28
Color	—	red	No
Odor	—	no	No
Floatables	—	no	No
pH	—	3.3	6–9
Iron (Fe)	mg dm⁻³	12.4	1
Copper (Cu)	mg dm⁻³	77	0.1
Nickel (Ni)	mg dm⁻³	0.13	0.1
Arsenic (As)	mg dm⁻³	<0.01	0.05
Zinc (Zn)	mg dm⁻³	1.2	1
Manganese (Mn)	mg dm⁻³	10	0.05
Aluminum (Al)	mg dm⁻³	0.094	—
Cadmium (Cd)	mg dm⁻³	<0.00050	0.01
Chrom (Cr)	mg dm⁻³	<1	—
Lead (Pb)	mg dm⁻³	<0.001	—
Arsenic (As)	mg dm⁻³	1	—
Cl⁻	mg dm⁻³	34	—
P₂O₅	mg dm⁻³	1.2	—
NO₃	mg dm⁻³	10	—

Table 2 Sieve analysis and apparent density.

Sieve analysis, mm	Quartz sand
	mass%
−4.00 + 2.362	47.65
+2.362	—
−2.363 + 1.700	20.35
−1.700 + 1.180	14.15
−1.180 + 0.850	6.80
−0.850 + 0.600	6.55
−0.600 + 0.425	4.50
−0.425 + 0.300	—
−0.300 + 0.212	—
−0.212 + 0	—
−0.212 + 0.15	—
−0.15 + 0.106	—
−0.106 + 0	—
Apparent density, g cm⁻³	1.495

iron, copper, aluminum, titanium and chrome are on the border of the sensitivity of the method of detection. Despite the fact that those metals are present in the form of oxides, and that AMD water is acidic, it is not possible to obtain leaching of those elements.

3.2 Metal removal using the sawdust from fir-wood and oak

3.2.1 Sawdust from fir-wood

The experimental procedure for the samples 1–6 was the same for all the samples, and only the contact time between

Table 3   Chemical analysis of quartz sand sample.

Element	Chemical content, mass%
Fe	0.090
Si	44.86
Mn	<0.0010
Mg	<0.003
Al	0.022
Ti	0.032
Ca	<0.0010
Cu	0.021
Cr	0.0076
V	<0.0030
Pb	<0.0010
Ni	<0.0010

Fig. 1   Adsorption degree of Cu and Zn using the sawdust from fir-wood.

Table 4   Concentration of elements and pH value of mine water at start and after the treatment using the sawdust from fir-wood.

Element	Experiment								
	Start	1	2	3	4	5	6	7	8
	Concentration, mg dm^{-3}								
Cu	77	7.5	3.35	1.48	3.7	1.6	1.3	57.1	18.8
Fe	12.4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	3.9	4.1
Mn	10	10.1	10	10.6	9.8	9.9	10	10.03	9.7
Zn	1.2	0.98	1.1	1.18	1.16	1.05	1.2	1.21	0.98
Ni	0.13	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	pH value								
		3.3	7.7	7.75	7.38	7.54	7.54	7.94	4.54	5.23

Table 5   Concentration of elements and pH value of mine water at start and after the treatment using the sawdust from oak.

Elements	Experiment				
	Start	9	10	11	12
	Concentration, mg dm^{-3}				
Cu	77	51.5	57.2	50.7	49.3
Fe	12.4	2.57	20.19	0.14	0.72
Mn	10	10.14	10.1	10.8	10.3
Zn	1.2	1.15	1.18	1.14	1.2
Ni	0.13	0.12	0.15	<0.1	<0.1
	pH value				
		3.3	3.1	3.04	3.19	3.19

the waste water and adsorbent was alternated. Contact time before the inlet of the effluent was 1, 2, 3, 4, 5 and 6 min for samples 1–6 respectively. The values of the heavy metals concentrations and pH values of the effluent are presented in Table 4. From results in Table 4, it is obvious that concentrations of iron and nickel are decreased to the values that are on the edge of the sensibility of used chemical method with the sawdust from fir-wood. Those values are significantly lower than those set by the legislation. The concentration of copper significantly decreased comparing to the starting value while the pH values increased. The concentration of zinc in the effluent is reduced during the experiments as well. The degree of adsorption (AD%) can be calculated by the equation:

$$AD \, (\%) = (1 - C(t)/C_i) * 100 \qquad (1)$$

C_i and $C(t)$ are the initial and actual concentration (g dm^{-3}) of metal in solution, respectively. The calculated results (eq. (1)) of adsorption degrees for copper and zinc are presented on Fig. 1. Analyzing Fig. 1, it is obvious that high rate of the copper adsorption is achieved (over 90%) in all of the samples. The highest adsorption value is achieved for the pH value of 7.94, and the adsorption degree was 98.31%. This value is acceptable for the release in the natural waterways (legislative for water class III and IV). The concentrations of iron and nickel were reduced below the
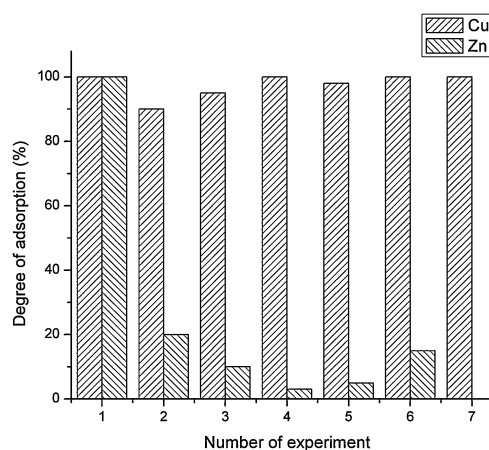
analytical method limit for the detection, and those values are significantly lower than those defined by law. The concentration of manganese was approximately unchanged trough the process.

In the experiments where the layers of quartz sand were positioned at the bottom of the column (experiments number 7 and 8), contact time between the waste water and material was very short, and the change in pH approximately the same as at the beginning of the experiment. This is a consequence of the fact that the flow rate of the waste water was very high. The degree of adsorption for copper was higher (75.6%) in experiment 7, and the pH value in this experiment increased. The adsorption degree of iron in both experiments was approximately the same (36%), while the concentrations of zinc and manganese were the same as in the initial solution.

3.2.2   Sawdust from oak

The contact time between the solid and liquid phase before the discharging the liquid, was 1, 2, 3 and 4 min for the experiments 9–12 respectively. The contact time for the experiments 11 and 12 was not extended as the pH vales for those experiments had the same value. The characterization of effluent in experiments 9–12 is summarized in Table 5.

The obtained results for the oak sample were not satisfying. The concentrations of copper and iron decreased at the end of the experiment, but not as in the case of samples treated with fir wood. The pH values of the starting waste

Table 6 Concentration of elements and pH value of mine water at start and after the treatment using cardboard.

		Experiment		
Elements	Start	13	14	15
		Concentration, mg dm^{-3}		
Cu	77	18.3	3.1	1.9
Fe	12.4	<0.01	<0.01	<0.01
Mn	10	10.3	10.8	10.3
Zn	1.2	1.04	0.91	0.87
Ni	0.13	<0.1	<0.1	<0.1
		pH value		
	3.3	6.83	7.93	7.93

water and final solution were the same that implies high material acidity. The concentrations of other elements were approximately the same as at the beginning. The obtained results for the experiments 11 and 12 for the adsorption of copper and iron were the same, and for these experiments the pH value of 3.19 is characteristic.

3.3 Cardboard

During the experiments 13, 14 and 15, cardboard was used as an adsorption material, and the contact time was 1, 2 and 3 min respectively. The concentration of elements and pH values of effluent are presented in Table 6. From the Table 6 it could be seen that the degree of copper reduction was between 70 mass% (experiment 13) and 95 mass% (experiment 15). The content of the iron was below the limit value for the detection of the applied chemical method for the detection. The amount of zinc was above the allowed value, although decreased comparing to the start and the amount of manganese was approximately the same trough the experiment.

Comparing the copper adsorption degree obtained by the cardboard as the adsorbent and the copper adsorption amount with the fir wood as the adsorbent, it is obvious that in both of cases values were very high and nearly identical (over 95%). However, the residual amounts of other metals in the water were above the allowed values for the mine water.

4. Conclusion

Sawdust and cardboard are the low cost, locally available material, and therefore could be used for the removal of heavy metals from the waste mine water. The sawdust was obtained from the oak and fir-wood. All adsorbing materials have shown good results for the removal of the iron. Good results were gained for the removal of zinc and nickel, and the best result for copper adsorption degree is achieved using the sawdust from fir-wood, which the value was 98.31%. The degree of copper reduction by cardboard was between 70 mass% and 95 mass% and the results are shown that the better result was achieved during the longer time contact between the cardboard and waste water. Manganese concentration in the effluent was the same as initial value using the different adsorption materials.

Acknowledgements

REFERENCES

1) M. G. King: JOM **59** (2007) 21–27.
2) F. Habashi: J. Mini. Metall. **43** (2007) 1–19.
3) D. Božić, V. Stanković, M. Gorgievski, G. Bogdanović and R. Kovačević: J. Hazard. Mater. **171** (2009) 684–692.
4) C. Namasivayam and K. Ranganathan: Environ. Technol. **16** (1995) 851–860.
5) K. Juttner, U. Galla and H. Schmieder: Electrochim. Acta **45** (2000) 2575–2594.
6) J. Dziewinski, S. Marczak, E. Nuttall, G. Purdy, W. Smith, J. Taylor and C. Zhou: Waste Management **18** (1998) 257–263.
7) L. J. J. Janssen and L. Koene: Chem. Eng. J. **85** (2002) 137–146.
8) R. Koivula, J. Lehto, L. Pajo, T. Gale and H. Leinonen: Hydrometallurgy **56** (2000) 93–108.
9) S. Chiarle and M. Ratto: Water Resources **34** (2000) 2971–2978.
10) G. Gupta and N. Torres: J. Hazard. Mater. **57** (1998) 243–248.
11) T. H. Baig, A. E. Garcia, K. J. Tierman and J. L. Gardea-Torresdey: Proc. 1999 Conference on Hazardous Waste Research, (1999) 131–139.
12) Z. Aksu and G. Dönmez: Process Biochem. **36** (2000) 451–458.
13) B. R. Reddy, N. Mirghaffari and I. Gaballah: Resources, Conservation and Recycling **21** (1997) 227–245.
14) B. Sandhya and T. Kurniawan: J. Hazard. Materials B **97** (2003) 219–243.
15) S. E. Bailey, T. J. Olin, R. M. Bricka and D. D. Adrian: Water Res. **33** (1999) 2469–2479.
16) D. Bozic, V. Stankovic, M. Gorgievski, G. Bogdanovic and R. Kovacevic: J. Hazard. Mater. **171** (2009) 684–692.
17) W. S. Wan Ngah and M. A. K. M. Hanafiah: Bioresource Technol. **99** (2008) 3935–3948.