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EDITOR

Snežana Šerbula

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PREFACE

The rapid development of industry and technology, the increased demand for using fossil fuels and exploitation of primary raw materials call into question sustainability of progress in today's society. Environmental research and ecological truth are the main subjects of the 26th International Conference Ecological Truth & Environmental Research 2018 (EcoTER'18), which will be held at Bor Lake, Serbia, 12-15 June 2018. On behalf of the Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the Conference.

The EcoTER'18 is organized by the Technical faculty in Bor, the University of Belgrade and co-organized by the Faculty of Technology, University of Banja Luka, the Faculty of Metallurgy and Technology, Podgorica, the Faculty of Metallurgy, Sisak and the Society of Young Researchers, Bor.

The primary goal of EcoTER'18 is to bring together academics, researchers, and industry engineers to exchange their experiences, expertise and ideas, and also to consider possibilities for collaborative research.

This year's conference is dedicated to the memory of Professor Zoran Marković, who organized the Conference for many years and who was one of our most loyal and active Committee members.

These proceedings include 77 papers from authors coming from universities, research institutes and industries in 13 countries: Argentina, Poland, Republic of Belarus, Turkey, France, Italia, Romania, Bulgaria, Croatia, Bosnia and Herzegovina, Macedonia, Montenegro, and Serbia.

Financial assistance provided by the Ministry of Education, Science and Technological Development of the Republic of Serbia is gratefully acknowledged. The support of the sponsors and their willingness and ability to cooperate has been of great importance for the success of EcoTER'18. The Organizing Committee would like to extend their appreciation and gratitude to all the sponsors and friends of the Conference for their donations and support.

We would like to thank all the authors who have contributed to these proceedings, and also to the members of the scientific and organizing committees, reviewer, speakers, chairpersons and all the Conference participants for their support to EcoTER'18. Sincere thanks to all the people who have contributed to the successful organization of EcoTER'18.

On behalf of the 26th EcoTER Organizing Committee,

Snežana Šerbula, PhD Full Professor

SORPTION OF COPPER BY FLY ASH

Sonja Milićević[1*], S. Martinović[2], M. Vlahović[2], N. Kanari[3], F. Diot[3], A. Popovic[1], M. Kojić[2], J. Yvon[3]

[1]Institute for Technology of Nuclear and Other Mineral Raw Materials, Franchet d'Esperey 86, Belgrade, SERBIA

[2]University of Belgrade, Institute of Chemistry, Technology and Metallurgy, 4 Karnegijeva St., Belgrade, SERBIA

[3]Université de Lorraine, UMR 7359 CNRS, CREGU, GeoRessources Laboratory, 2, rue du doyen Roubault, BP 10162, 54505 Vandoeuvre-lès-Nancy, FRANCE

*s.milicevic@itnms.ac.rs

Abstract

This study is occupied by using fly ash for copper removal from the acid mine wastewater and synthetic solution of the similar composition. Chemical analysis of mine wastewater proved that the values of Cu, Zn, Fe, and Mn exceed the maximum accepted concentration in a large extent. Serbian fly ash from "Nikola Tesla" power plant was used as a low cost sorbent for removal of copper ions (Cu^{2+}) from aqueous solutions. Fly ash was subjected to the elementary and XRD analysis. As a method, batch sorption procedure was applied. Sorption efficiency was studied as a function of the contact time, and amount of the sorbent. Equilibrium was determined after 90 min for all investigated sorbent dosages.

Keywords: Copper, Sorption, Fly ash

INTRODUCTION

Heavy metals are released into the environment finding the way to get into the water-streams and thus make an environmental contamination that presents threat to humans, animals, and plants. This can cause serious diseases and complex disorders [1].

Acid mine waste water (drainage) is significant environmental problem since it contains high concentration of toxic and heavy metals such as copper, nickel, cadmium, lead, iron, manganese, and zinc. Amount of these metals exceed maximum acceptable concentration (MAC). Today, heavy metals are most serious pollutants, becoming a severe public health problem. During the mining process of copper exploitation, large amount of waste water is generated. The chemical composition of these waste streams is very complicated and depends on the chemical composition of the ore that leaches during the exploitation. At the Cerovo and Krivelj deposits, RBB-RTB Bor, one of the biggest problems presents the generated lake at the open pit. At this moment, the estimated amount of the "Cerovo lake" is 600.000.000 dm^3 (and it grows every day) of this water with the average content of 200 mg Cu^{2+}/dm^3. The mathematical calculation leads us to the fact that only in this lake 120 tonnes of copper is trapped [1,2].

Concentrations of heavy metals in the wastewater and water-streams have to be reduced in order to satisfy rigid legislative standards. They can be removed by various technologies, most often expensive or inefficient and technically complicated especially because of limited maximum accepted concentrations required by the EPA (Environmental Protection Agency) [1-3]. The conventional techniques for heavy metals removing from aqueous solutions include oxidation, reduction, chemical precipitation, filtration, ion exchange, adsorption, membrane techniques, electrolytic or liquid extraction, reverse osmosis, biological process [3,4].

Each of these methods is used only in special cases since it has some limitations in practice [4,5]. Namely, the major disadvantages of almost mentioned methods are production of new hazardous waste, mostly solid, at the end of the treatment as well as high cost of sorbent and applied technique [1]. Among these processes, the adsorption is a simple and effective technique for the removal of heavy metals form wastewater. Nowadays, many researchers are occupied by development of new low cost materials and methods for the treatment of wastewater containing heavy metals, for example natural adsorbents such are zeolites, wood, lignite, metal oxides, fly ash, coal, and waste biomass [1,4,5]. In general, sorbent can be characterized as a low cost if it requires little processing, is abundant in nature or is a by-product of industrial activities. Hence, industrial by-products are almost zero-cost materials and at the same time their utilization could contribute to the solution of their management problem improving the material efficiency within the several industrial activities. Predominant mechanism in this process is ion exchange, but also there is surface adsorption, chemisorption, complexation and adsorption-complexation [1-5].

Fly ash has potential application in wastewater treatment because of its major chemical components (alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon), and its physical properties such as porosity, particle size distribution and surface area. Besides, the alkaline nature of fly ash makes it a good neutralizing agent [1,2]. Namely, fly ash as a potential hazardous solid waste produced like a by-product in power plants worldwide in million tonnes has attracted researches interest for years.

The objective of this study is possibility of using domestic fly ash on ability for removing the heavy metals from synthetic aqueous solution and acid waste drainage water. Batch sorption experiments were conducted to characterize and model the sorption equilibrium.

Since the copper industry is one of the biggest in the field of the heavy metals and, at the same, there is a big copper producing facility RTB Bor in Serbia, the main accent in this paper, was put specifically on the removal of this metal.

MATERIALS AND METHODS

Sample characterization

The fly ash used in the experiments was collected in power plant Nikola Tesla, Obrenovac, without any pre-treatment. It remains as a residue from lignite combustion recovered from cyclones and electrostatic filters of the power plant.

Chemical and XRD analysis of the fly ash were done and shown in this paper. The XRD method was used to determine the phase composition. The XRD patterns were obtained on a Philips PW 1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter. The diffraction data were collected in the 2θ Bragg angle range from 4 to 65^o, counting for 0.5 s (qualitative identification) at every 0.02^o step. The divergence and receiving slits were fixed 1 and 0.1, respectively. All the XRD measurements were performed at room temperature in a stationary sample holder.

Mining wastewater originated from the generated lake at the open pit Cerovo deposit, RBB-RTB Bor. Synthetic aqueous solution was prepared too by dissolving the appropriate amount of $CuSO_4$ in deionized water.

Sorption experiments

The kinetic experiments were performed at room temperature using the batch technique under the continuous stirring conditions. The procedure was as follows: weighted amount of sorbent was placed into a glass vessel with cover. Prepared synthetic or "real" solution was added. Volume of the solutions was constant (100 dm^3), as well as the stirring conditions. The effectiveness of different amounts of sorbent was observed during the experiment (2, 6, and 10 g of fly ash). Experiments were monitored periodically up to 120 min. In order to quantify sorption efficiency, suspension was filtered and residual copper concentration in the filtrate was determined by Perkin Elmer Atomic Adsorption Spectroscopy, type "PinAAcle 900T (Perkin Elmer)" instrument.

RESULTS AND DISCUSSION

Characterization of wastewater

Almost all previous researches were occupied with the sorption of heavy metals realized by usage of synthetic solutions. However, the real problem arises in case when the heavy metals should be removed from the real system of mining wastewater.

Chemical analysis of acid mine wastewater located at "Cerovo Lake" is shown in Table 1.

Table 1 *Chemical analysis of acid mine waste water*

Content (mg/dm^3)												
Fe	Mn	Zn	Cu	Pb	Ni	Cd	Cr	Cl^-	SO_4^{2-}	SiO_2	CaO	MgO
70.5	30.0	50.0	168.0	0.8	0.5	0.36	0.01	0.018	3.69	87.76	601.66	543.0

Analyzed wastewater is acid aqueous solution with pH of 3.15.

Chemical analysis of synthetic aqueous solution that imitated the real wastewater is given in Table 2. pH of the synthetic aqueous solution was 2.87.

Table 2 *Chemical composition of synthetic aqueous solution*

Content (mg/dm^3)			
Fe	Mn	Zn	Cu
70.6	34	49.5	171

Characterization of sorbent

Chemical composition of fly ash is shown in Table 3. The results of chemical analysis showed that the main and most important components of the fly ash are silica, alumina, as well as calcium and iron oxides with smaller amounts of magnesium, alkalies, and traces of many other elements.

***Table 3** Chemical composition of fly ash*

Content (%)							
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2
47.8	30.53	5.47	8.69	2.29	1.49	0.25	1.02
Cd	Pb	Zn	Cu	Cr	Ni	Mn	LOI
0.005	0.04	0.021	0.005	0.022	0.03	0.045	1.45

XRD analysis of fly ash was done and results showed presence of quartz, mullite, and plagioclase, Figure 1.

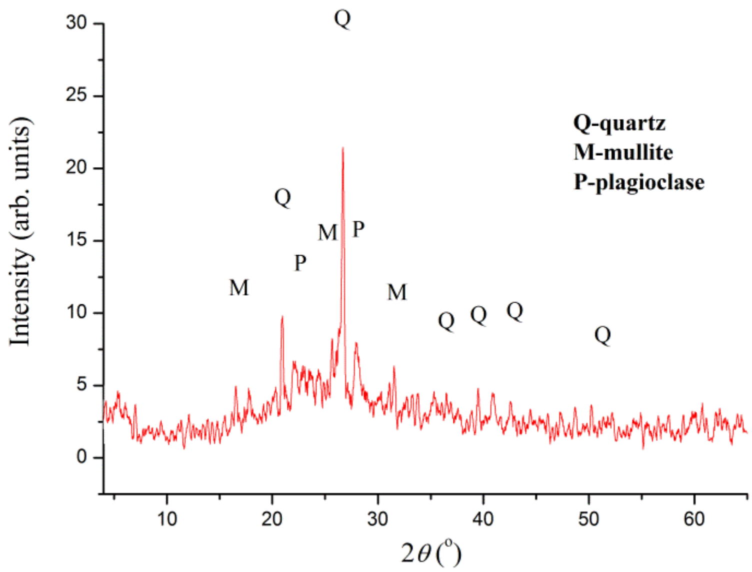

***Figure 1** XRD pattern of fly ash*

The major mineral phase is quartz, while the mullite and plagioclase are present as an accessory minerals and their effect on physicochemical behavior of the minerals are limited. The presence of magnetic phase was detected in analyzed sample, but there was no one reflection to match this phase. Since the level of crystallinity is very small, portion of amorphous phase is significant.

Kinetics experiments

The effects of sorbent dosage and contact time on sorption process at 20 ± 2°C were studied. Initial batch studies conducted to assess the time taken for the equilibrium to be attained. The solution-sorbent mixtures were shaken and at the end of predetermined time intervals (5, 30, 60, 90, and 120 minutes) their content was filtered and the filtrates were analyzed for the content of Cu. The influence of the other present metals will be investigated and analysed in some further papers.

As it presented, the sorption of Cu onto fly ash showed typical two phases kinetics with rapid sorption period during the first 5 minutes followed by a slower one. During the initial stage of sorption, a large number of surface free sites are available for sorption whereas, with gradual occupancy of these sites during the sorption process, it becomes difficult to be attracted to the sorbent due to repulsive forces between the sorbate molecules on solid surface and in the liquid solution. Besides, a driving force of mass transfer between the liquid phase and the solid phase of fly ash decreases with the time, which also results in the slowing down of the sorption during the later phase of sorption. The chemical constituents of fly ash affect its sorptive properties towards metal cation. Therefore, an attempt was made to establish a relationship between the sorption capacity of the fly ash and its major chemical constituents, such as mineral oxides (calcium, aluminium, and silica oxides) and carbon. As assumed herein, the fly ash is a dual sorbent that means it sorbs by both mineral and carbon. Copper removal by fly ash was achieved through the competitive sorption between carbon and mineral [3].

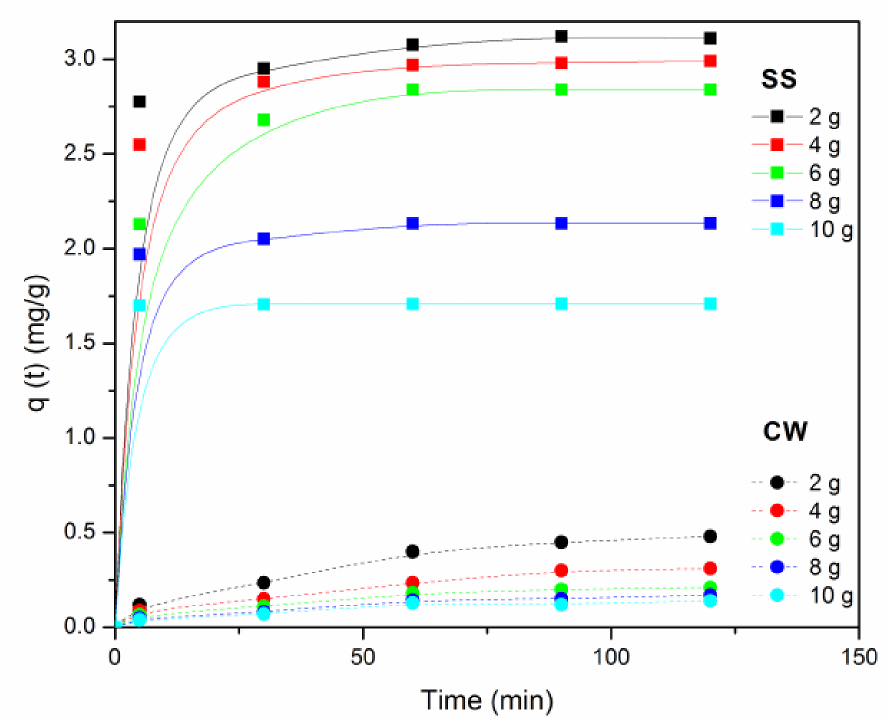

Figure 2 *Sorption of Cu on fly ash from complex aqueous solutions (SS-synthetic solution and CW-Cerovo Wastewater) depending on time*

The effect of sorbent dose on the removal of heavy metals shown in Figure 2 displays that sorption capacity, as expected, decreases with sorbent dosage. The higher amount of the sorbent results in a better Cu removal. However, due to the higher competitiveness of the active centers for the sorption, the sorption capacity decrease.

The sorption of copper from the synthetic solution was significantly higher compared with the sorption from the real wastewater. This is mainly due to the presence of many other ions that are presented in a real wastewater, unlike the synthetic solution. In order to increase the effectiveness of the removal from the real wastewater, certain pretreatment should be considered in a future.

CONCLUSION

This work concerns the removal of Cu^{2+} ions from the multi-complex solutions by fly ash. The influence of two parameters (fly ash dosage and contact time) on the removal of heavy metal ions commonly encountered in mining wastewater was reported. It was found that copper was sorbed onto the fly ash very rapidly (within the first 30 min), while the equilibrium was reached in 90 minutes. Higher dosage of the sorbent leads to higher effectiveness and the lower sorption capacity.

Sorption efficiency of all tested metals dosages was considerably higher in a synthetic solution compared to the real system.

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