INTERNATIONAL SCIENCE CONFERENCE REPORTING FOR SUSTAINABILITY

Conference Proceedings

7th – 10th of MAY 2013, BEČIĆI, MONTENEGRO

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CONCENTRATION METHOD FOR THE MINING WASTEWATER – VALORIZATION OF THE COPPER

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Abstract

During the mining process of copper exploitation a large amount of wastewater is generated. Not only do the copper ions contaminate the water but also represent a great loss for the copper production industry. Negative charged surface of zeolite has been used for adsorption of copper. The batch and dynamic experiments have been conducted. After the adsorption the zeolite has been regenerated with the concentrated solution of Na-salt. The volume of the regenerative solution is 30 times smaller compared to the total amount of the waste solution that has been purified and the concentration of the obtained solution is 12 g Cu^{2+}/dm^3.

Keywords: zeolite, copper, adsorption, regeneration, valorization

Introduction

Heavy metals are among the prior toxic pollutants in wastewater and represent a serious threat to soil and water pollution. Although there are many sources of heavy metals, specific industrial sectors are, at present, those which mostly contribute to environmental pollution with these toxic metals[1]. Copper has been reported as one of the most widely used heavy metals in electrical and electroplating industries. Since copper is not biodegradable and is an essential metal in a number of enzymes of all forms of life, problems arise when it is deficient or in excess[2].

One of the largest copper production plants in Europe with the total copper production of 35 000 - 40 000 t per year is RTB BOR situated in Bor, Serbia. During the mining process of copper exploitation, large amounts of waste water are 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. The major problem are the copper ions that not only contaminate the water but also represent a loss for the copper production industry.

At the Cerovo Deposit, RBB-RTB, the generated lake at the open pit represents one of the biggest problems. 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. According to a simple mathematical calculation, only in "Cerovo Lake" 120 tones of copper is trapped. With current official price of 8.000 $/ton this makes a total of 960.000 $. Besides this lake, at the RTB Bor plants plenty of "copper wastewater reservoirs" exist that, although not so large, still have a higher copper content.

The applied purifying technology is not only supposed to remove the copper but also to provide the possibility to valorize this highly valuable metal. On the other hand, the technology needs to be a low cost one, effective and environmentally friendly.

Among these numerous techniques used, adsorption has gained a lot of attention recently, as eco-friendly, cost effective and easy operational technology.

Natural materials that are available in large quantities may have potential as inexpensive sorbents. One of potential adsorbents that could meet all these requests is zeolite. Zeolites have been widely used in heavy metals adsorption experiments because of their unique physical and chemical properties (crystallinity, thermal stability, well defined cage structure of molecular size, ion exchange, good hydrodynamic properties, etc)[3]. Among many natural zeolites, clinoptilolite is the most abundant. It's a common alteration product of vitroclastic sediments that have been diagenetically altered in subaerial and marine environments[4]. Zeolites are hydrated aluminosilicates of alkali and alkaline earth elements with unique crystal structures. As it is well known, the primary building units of the aluminosilicates are the TO_4 tetrahedra, where T is Si or Al. Tetrahedra are linked so as to make structure of zeolite rich with channels and cavities[5]. Each aluminum ion that is present in the zeolite framework yields a net negative charge[6]. This porous, negatively charged surface of zeolite can be used for adsorption of metals such as copper and zinc. Negative charge surface is balanced by mono and divalent exchangeable cations such as Na, Ca, K and Mg that give zeolite high cation exchange capacity (CEC).

The objective of these investigations was to determine the optimal parameters for the adsorption and then to optimize the regeneration process in order to obtain the least volume of the effluent with highest copper content.

Experiments

A clinoptilolite-rich zeolite tuff was obtained from the Zlatokop Deposit in Vranjska Banja, Serbia. According to X-ray powder diffraction (XRPD) analysis, the clinoptilolite content is ~80% and the main impurities in the zeolite are quartz, feldspar and carbonate. The total cation exchange capacity (CEC) of the zeolitic tuff was 146 meq/100 g, measured with 1 M NH_4Cl. For the adsorption experiments the zeolite sample was ground and sieved to particle sizes -0,043mm and -0.8+0.6mm.

The examination of copper uptake was preformed in both batch and fixed bed mode.

The experiments using batch technique were carried out by shaking 1g of zeolite (-0.043mm) with 100 cm^3 aqueous solution of $CuSO_4 \cdot 5H_2O$ containing various initial copper concentrations (1-14 Cu^{2+} mmol/l). After equilibration the suspensions were filtered and in supernatants the concentration of remaining copper was determined by atomic absorption spectrophotometry.

The experiments using fixed bed technique were performed not in a column but in a square shape vessel, imitating the micro system of the large pools. The total amount of the zeolite was 800 g (-0.8+0.6mm). The contact time was 20 min and the concentration of the influent was 300 mg Cu^{2+}/l.

The regeneration process was also performed in a fixed bed technique with 15g/l solution of Na_2SO_4. The passing of the solution in both the adsorption and the regeneration cycle was adverse from the bottom to the top, where the overflow was collected and tested for the present of the Cu^{2+} by atomic absorption spectrophotometry.

Results and Discussion

Copper adsorption by zeolite was examined using extended range of initial Cu concentration. The experimental data from the equilibrium studies were analyzed using Langmuir and Freundlich sorption models and better fit of experimental data was obtained by using Freundlich model.

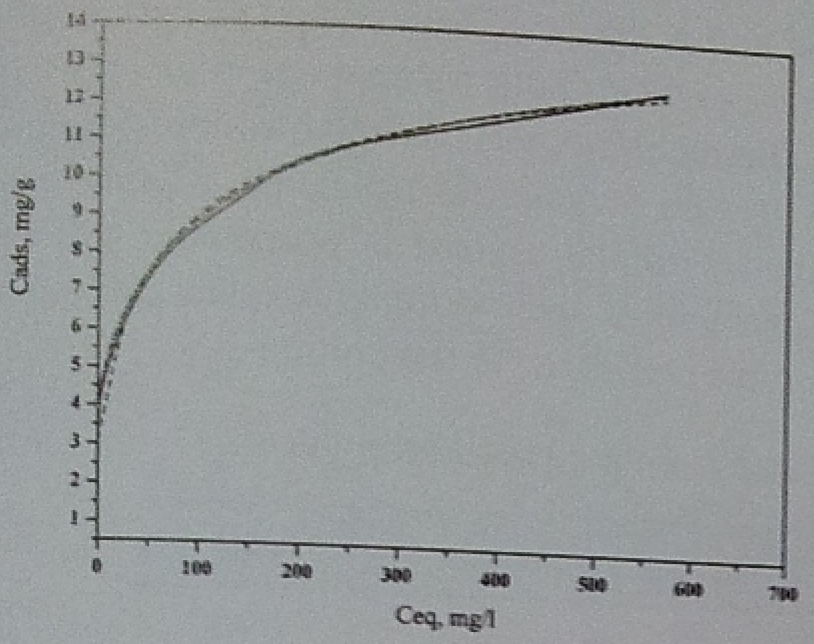

Figure 1 Sorption isotherms of copper uptake on zeolite

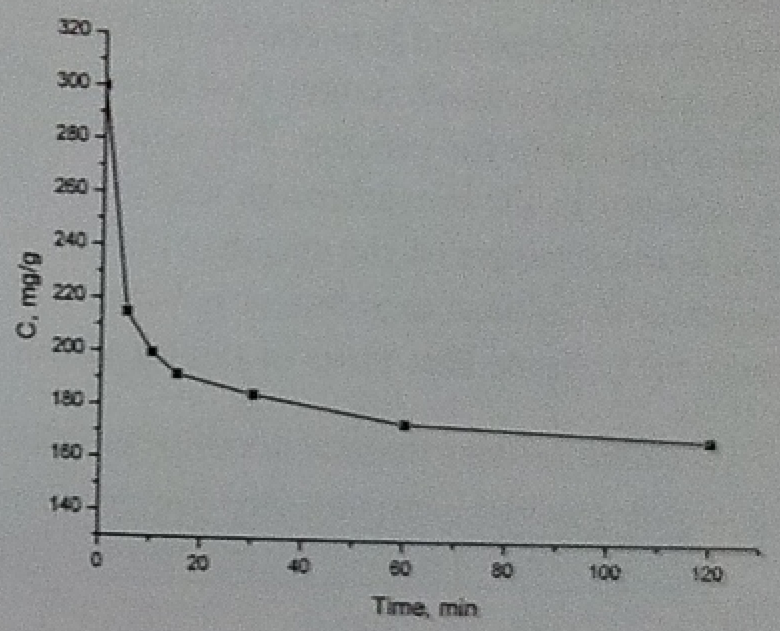

Figure 2 Kinetics of copper sorption on zeolite

The sorption capacity q_m, which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage, showed that a mass capacity for the Cu^{2+}, uptake by zeolite is 12.2 mg/g.

Preliminary kinetic experiments have shown that most of the contaminants have been sorbed on the natural zeolite within first 20 minutes, while the plateau has been achieved after 60 minutes.

Based on kinetic experiments we accepted 20 minutes as the optimal contact time for the experiments in fixed bed mode. The obtained results are presented in Figure 3. The concentration of the influent was 300 mg/l.

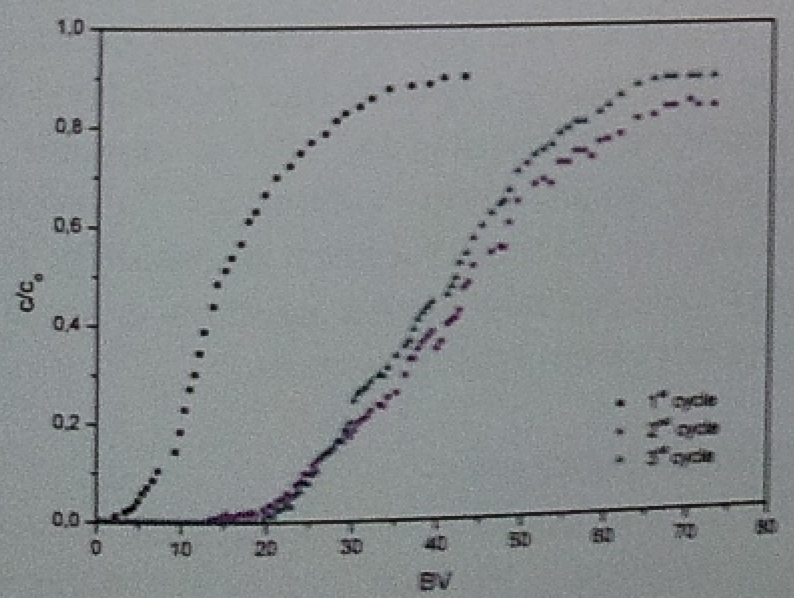

Figure 3 Breakthrough curves for the adsorption cycles

The breakthrough curves in Figure 3 differ from those obtained in the classic column experiments. The typical S-shape remains but the slope is not so sharp i.e. after the breakthrough it takes more time to reach the exhaustion point. The big difference in the breakthrough point can be observed between the first exchange cycle and the next one, after the regeneration of the zeolite. This can be attributed to the fact that after the regeneration zeolite is in monoionic form and that reduces the influence and the interference of other cations. Further, the obstructions caused by the impurities present in zeolite are likely to be removed after the first usage cycle and regeneration.

After the first adsorption cycle the breakthrough curve moves towards the higher values of BV i.e. capacity. From Figure 3 it can be concluded that the 2nd and the 3rd cycle remain almost unchanged. The breakthrough point is 20BV and the exhaustion point at 60BV.

For the column experiments, the difference between the breakthrough and exhaustion point is usually much smaller due to the sharp slope. The benefit of the standard column experiments is equal feeding and saturation of the adsorption material. With fixed bed layer like this, due to the square shape and much larger base area, the feeding is not even and potential saturation gradient occurs. Due to this gradient the slope is not sharp and the period between the breakthrough and exhaustion is much longer than in the regular experiments with the column. The ratio between the capacity in the breakthrough and exhaustion point is the measure of the system effectiveness. This ratio in column experiment is better as it is closer to 1. Since this ratio in our experiments was 0.61 (Table 1) we could say that this system is not highly effective, but, in the real systems the amount of the mining waste water is so large that no column system is acceptable and possible. Due to this fact we find that the effectiveness of this continual system is acceptable and the construction of such systems is easier and more favorable compared to the column.

Table 1 Experimental conditions and data calculated from the breakthrough curve

C_0,mg/l	m, g	V_b, ml	q_b, mg/g	V_e, ml	q_e,mg/g	η
300.0	800.0	25	9.4	60	15.3	0.61

After reaching the exhaustion point the same mass of zeolite was treated with the concentrated solution of Na_2SO_4 (15g/l), with the same flow as the adsorption cycle. The obtained results are presented in Figure 4. The regeneration was a rapid process where the total amount of copper was exchanged with less than 3l of Na_2SO_4.

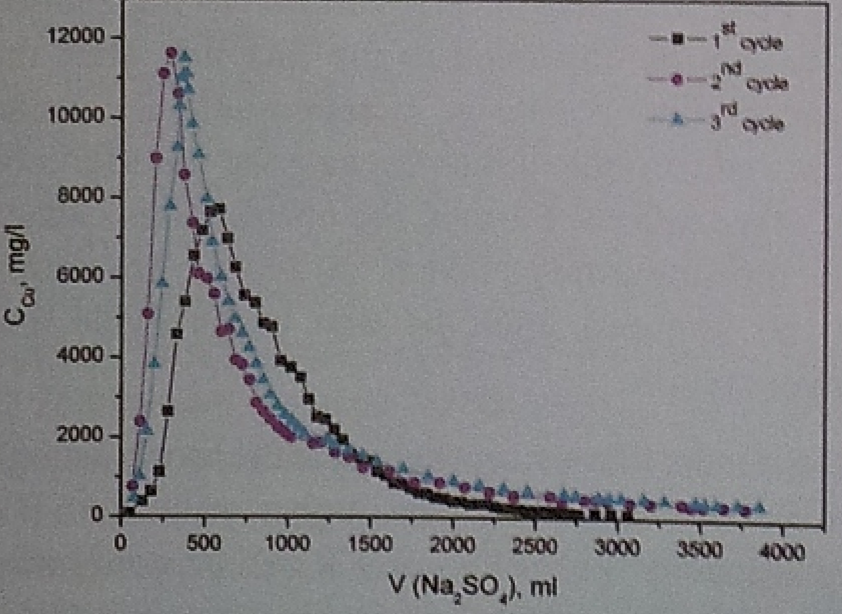

Figure 4 Regeneration curves

From Figure 4 we can see that most of the copper was regenerated within the first 2l. This means that the copper from 60l of solution was extracted to highly concentrated solution, up to 12g Cu^{2+}/l, with the total volume that was 30 times smaller compared to the amount of the solution that was purified.

Conclusions

Zeolite can be efficiently used for the adsorption of copper ions. According to the batch experiments maximum sorption capacity for the copper is 12.2 mg/g. The adsorption process is a very fast one whereby the most of copper ions are sorbed on the natural zeolite within first 20 minutes. This time has been chosen to be the optimum contact time in the experiments under dynamic conditions. The experiments in fixed bed have shown that zeolite can be efficiently used more than a several times and that sorption capacity does not decrease, but on the contrary, improves. The system like this is less efficient than the one with the column, but the construction of such a system is easier and cost effective. The major benefit is presented in the fact that the system like this retains the regeneration efficiency and that is possible to obtain 30 times lower volume of the copper solution with 40 times higher concentration. This highly concentrated copper solution is suitable for further electrolysis treatment.

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