TREATMENT OF MINE WATERS FROM ACID MINE DRAINAGES BY ADSORPTION ON NATURAL ADSORBENTS

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ABSTRACT. Active or closed copper mines pollute the environment for many years by self-leaching of residual minerals from ore bodies or from dam constructed nearby the mine, forming mine waters that contain a reasonably high concentration of copper but also some other heavy metals and as a rule sulphuric acid. Formed seepages bring out mine waters, damaging surrounding surface waters and soil. Adsorption of heavy metal ions by natural adsorbents appears to be a new possibility for treating such kind of mine waters. Sawdust and wheat straw as by-products of wood and agriculture were studied for the adsorption of heavy metals from acid mine drainages (AMDs) of closed copper mine „Cerovo" Bor, Serbia. In this work are presented some results on the column adsorption of heavy metal ions from an AMD. Change of pH during the adsorption process is considered as well. *The results showed that the column adsorption can successfully be used for metal ions removal from mine waters achieving a high adsorption degree – higher than 99%.* Instead of desorption, the loaded adsorbent was drained, dried and burned; the metal bearing ash was leached with a small volume of sulphuric acid solution to concentrate metal therein. Obtained leach solution is suitable for treating by the electrowinning in order to remove and recovery of copper, rounding off the technological process. A new, possible technology for mine waters treatment and metal recovery was proposed and considered in its particular stages.

Keywords: mine water, adsorption, leaching, copper, sawdust

ОБРАБОТКА НА ВОДИ ОТ КИСЕЛИННИ МИННИ ДРЕНАЖИ ЧРЕЗ АДСОРБЦИЯ С НАТУРАЛНИ АДСОРБЕНТИ

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РЕЗЮМЕ. Работещите или закритите вече медни рудници замърсяват с години околната среда чрез самоизлужване на утаечни материали от рудното тяло или прегради в близост до мините, образуващи води с висока концентрация на мед и други тежки метали, както и сярна киселина. Образуваното количество течност просмукало се през порите уврежда околната вода на повърхността и почвата. Адсорбцията на тежки метални йони от натурални адсорбенти се оказва една нова възможност за третиране на подобен вид води. Дървените трици и пшеничната слама, които са отпадни продукти от дърводобива и земеделието, са изследвани като адсорбенти на тежки метали от киселинни минни дренажи (КМД) в закритата вече медна мина „ Церово" в гр. Бор, Сърбия. Статията представя някои резултати от адсорбцията на йони на тежки метали от КМД. Отчетена е също така и промяната на pH по време на адсорбциата. Получените резултати показват, че подобен тип адсорбция може да бъде използвана за отстраняване на метални йони , достигайки висока степен от порядъка на 99%. Използваният адсорбент е дрениран, изсушени изгорян; пепелта съдържаща метала, се излужва с помощта на незначително количество разтвор на сярна киселина с цел концентриране съдържанието на метала. Полученият разтвор е подходящ за електролитно отделяне на медта, като по този начин се затваря технологичния процес. Предложена е нова технология за третиране на минни води и извличане на метали, описана на различни етапи.

Ключови думи: вода от мините, адсорбция , излужване, мед , дървени трици.

Introduction

Pollution of the environment by toxic metal ions is a paramount world problem, caused by industrial activities such as mining, extractive metallurgy as well as metal working industry. Numerous technologies have been developed for treating wastewaters with low concentrations of metal. They include chemical precipitation, electrowinning or cementation of the ions present in wastewaters, adsorption and ion-exchange, reverse osmosis, electrodialysis, and other membrane separation techniques. These methods, however, have shown different effectiveness but, as a rule, they are not able to remove traces of metal ions and to reach a desired low level of metal in exit stream. In some cases an excessive amount of chemicals or energy has to be spent meaning high operating costs. This is why many efforts have been done in developing advanced more efficient and less expensive technologies for such wastewaters purification. Especial attention has been paid to the adsorption using „low-cost"adsorbents [1]. Recently, it was found that many by-products and waste materials from agriculture or timber industry that are no economically valuable are able to adsorb metal ions to a certain extent. Different materials were tested as potentially possible low-cost sorbents as: walnut and nut shells, spent grains, olive stones, peanut skins, onion and orange peals, rice husks, leaves, coffee and tea waste, tree fern and other similar plant waste materials [1,2]. Adsorption on natural adsorbents like wood sawdust, wood bark, wheat straw, corn or sunflower stalks and similar materials appear to be very convenient adsorbents for immobilization of different metal ions onto these adsorbents, particularly from very dilute effluents containing a few ppms of hazardous ions only. Other, natural materials were also considered for the same purpose, such as: peat, lignite, bentonite and clay, lignocellulosic materials, shell egg membrane, fly ash, marine algae and alginates and many others [2].

Sawdust, having a great potential as an adsorbent, has attracted more attention of scientists dealing with different aspects of wastewater purification by biosorption. If sawdust could be used as absorbent, both environment protection and wood industry or agriculture would benefit: effluent solutions containing heavy metals would be cleaned by a cheap adsorbent and a new market for sawdust and similar waste materials would be opened. Current researches have been performed with sawdust produced from different kind of trees, mainly from local both coniferous or deciduous forests and some others more or less exotic trees depending on the country where the experiments were realised [1-3]. It was pointed out that metal adsorption depends essentially upon three main parameters: the nature of adsorbent, the kind of heavy metal ions and on the initial pH of solution.

In this study mine water from ex-open pit „Cerovo"of Copper Mining & Smelting Co. (RTB) Bor, Serbia was used as a model-system for the removal of heavy metal ions by means of adsorption on sawdust and wheat straw.

The main streams of mine waters in copper mines of RTB are water springs appearing in underground mine that have to be pumped-up from the mine providing normal working condition down in the cave; acid mine drainages (AMDs) seeping from the inner lateral slopes of open pits accumulated at the pit bottoms, or from the outer flowing down and polluting surrounding surface waters or soil making them unsuitable for usage. Such waters contain a certain amount of metal ion, particularly Cu^{2+}, Fe^{2+}/Fe^{3+}, Zn^{2+}, sometimes in considerable concentration as well as sulphuric acid, as it is illustrated in Table 1, just for one of the existing copper mines - closed open pit called „Cerovo".

Table 1. Composition of AMDs of copper mine „Cerovo"

Metal	Spring 1 (mgdm^{-3})	Spring 2 (mgdm^{-3})	"Ecology Dam" (mgdm^{-3})	Max allowed concentration, (mgdm^{-3})
Mn	40.1	65.7	9.7	/
Cu	1050	1550	132.45	0.1
Fe	< 10	< 10	0.14	
Ni	0.5	1.1	0.07	0.05
Co	2.1	5.6	0.32	0.2
Cd	0.2	0.4	0.05	0.005
Zn	> 20	> 27	5.7	0.2
Be	0.003	0.074	0.009	0.0002

There are three sources of mine waters from this closed open pit, having different composition and different potential in the sense of flow-rate. The source "Ecology Dam" is a small lake and has the greatest potential. Springs 1 and 2 both contain high concentration of Cu^{2+} but they have low capacity - only few dm^3/min. All three sources have unexpectedly low concentration of iron while zinc concentration is quite high. For this study mine water from "Ecology Dam" was chosen because it is more suitable for adsorption than waters from the other two springs.

Experimental

Materials and methods

A series of experiments were firstly performed by using synthetic single ion solutions (Cu^{2+}, Ni^{2+} and Zn^{2+}) prepared by dissolving corresponding metal salts (AnalaR quality) in distilled water. Prepared stock solutions (concentration 200 mg dm^{-3}) were further diluted if it was needed and used in the column adsorption experiments. Two kinds of adsorbents were used in these experiments: wheat straw and beech sawdust. Both adsorbents were firstly grinded, than sieved through set of laboratory sieves and only the sieve fraction (-1 + 0.4 mm) was used in the experiments. No any other pre-treatment of the adsorbents has been performed. The concentrations of considered heavy metal ion during experiments were determined by periodical sampling the treated solution and analyzing the samples by employing an atomic adsorption spectrophotometer (Perkin-Elmer – 403). Change of pH values during adsorption was periodically measured by a WinoLab - 720 pH-meters.

Experimental procedure

Column adsorption experiments were performed in a plexi-glass column (inner diameter 32 mm and height 500 mm). At the bottom of the column was mounted a glass tap for adjusting the flow rate through the column. Above the tap was placed a layer of glass wool in order to prevent adsorbent particles to leave the column. Above the protective glass wool layer a fixed bed of beech sawdust or wheat straw was formed. Above the bed of the used adsorbent was placed another glass wool layer to provide uniform flow distribution across the whole cross sectional area of the column, preventing the formation of channels and stagnant – non-wetable zones inside the bed. Prior the adsorption a portion of distilled water passed through the bed washing out very fine particles from the bed. After rinsing and drainage the column, the experiment was started by feeding the column with chosen synthetic solution of considered metal ion. Volume of the aqueous phase passed through the column was an independent variable.

After passing a certain volume of the aqueous phase through the column, samples were taken for both the analysis on residual metal content and measuring the current pH value. After finishing the adsorption experiment, the loaded adsorbent was drained, taken from the column, dried on air and burned. The ash was further annealed at 800°C to complete the combustion of residual carbon. After cooling the ash it was leached with as smaller as possible volume of 0.5 M H_2SO_4. Leach solution was filtered and analyzed on the content of metal ions. Column adsorption experiments were carried out at ambient temperature and at constant flow-rate of 10 ml/min

Results and disscusion

Behaviour of the initial pH with volume passed through the column

Changes of the initial pH of treated solution against the volume of the solution passed through the column, in the adsorption experiments, using beech sawdust as an adsorbent, is presented in Fig. 1. Identical shape of the curves and behaviour against volume passed through was obtained for the wheat straw, too. It can be seen from the Fig. 1, that a sharp increase appears at the beginning of the process indicating a simultaneous adsorption of H^+ and the adsorbing metal ions reaching a constant value just after 0.1 - 0.2 dm^{-3} of the volume passed through the column and does not change anymore. Most authors supposed an ion exchange mechanism when alkali and alkali-earth atoms from adsorbent molecular structure are substituted by metal and hydrogen ions [4]. Increasing of pH during adsorption could be considered as a good adsorbent feature because partial neutralization of treated solution occurs in parallel with the adsorption process what could simplify the purification process technology because no additional adjusting of pH is needed.

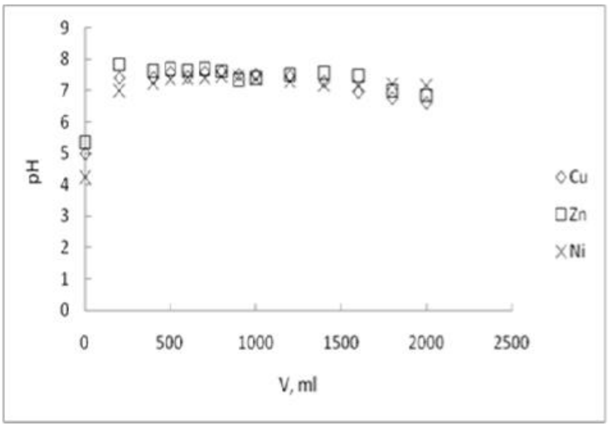

Fig. 1 Change of initial pH value vs. volume of aqueous solution passed through the column: beech sawdust; m=85 g;

Breakthrough curves

Column adsorption breakthrough curves, for all three investigated ions are shown in Fig. 2, in which normalized concentration change for each metal ion is plotted against the volume of the solution passed through the column. It is clearly shown that the breakthrough points appear earlier for nickel and zinc while later for copper meaning a higher adsorption capacity of the sawdust against this ion than against the other two. Wheat straw showed that the breakthrough points are almost equal for zinc and copper, but smaller for nickel.

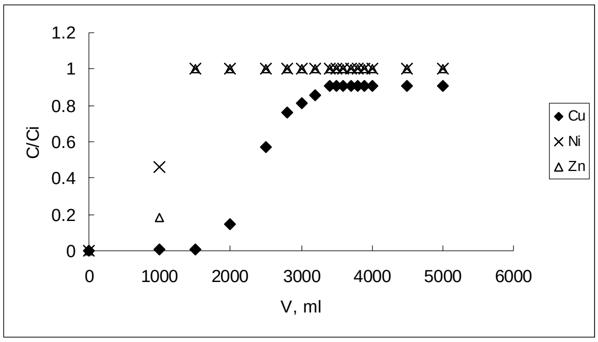

Fig.2 Breakthrough curves vs. volume passed through the column; C_i=0.2 gdm^{-3}; beech sawdust m=85 g

Results, obtained for the column adsorption of copper from a single ion solution with the concentration of copper ions approximately equal as the concentration of mine water as well as from mine water itself, are presented in Fig. 3. The breakthrough point appears almost at the same volume in both cases. It means that the adsorption of copper ions from mine water will be predominant comparing to the other present and here particularly considered ions.

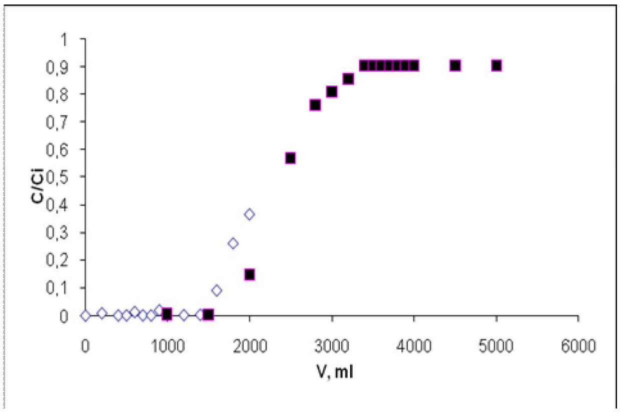

Fig. 3 Breakthrough curves for column adsorption of copper from: ◊- single ion solution and ■- mine water

Block diagram of the proposed adsorption process

Based on the experiments here described and exposed results as well as on the previously reported investigation a sketch of the process for mine waters liberation from copper ions was proposed and presented in the form of block diagram I n Fig. 4

The proposed technological process consists of several stages and represents the basic processes and unit operations that would be used in the process which should result in both the reduction of acidity of mining waters and in removal of copper as the most valuable metal in the considered mine waters. The process consists from the column adsorption on sawdust or on wheat straw as low-cost adsorbent as the first and most important step. Instead of desorption, it was proposed burning, recuperation of generated heat for internal needs; produced ash leaching with sulphuric acid solution, and treatment of the leaching solution by electrowinning for recovery of copper concentrated in.

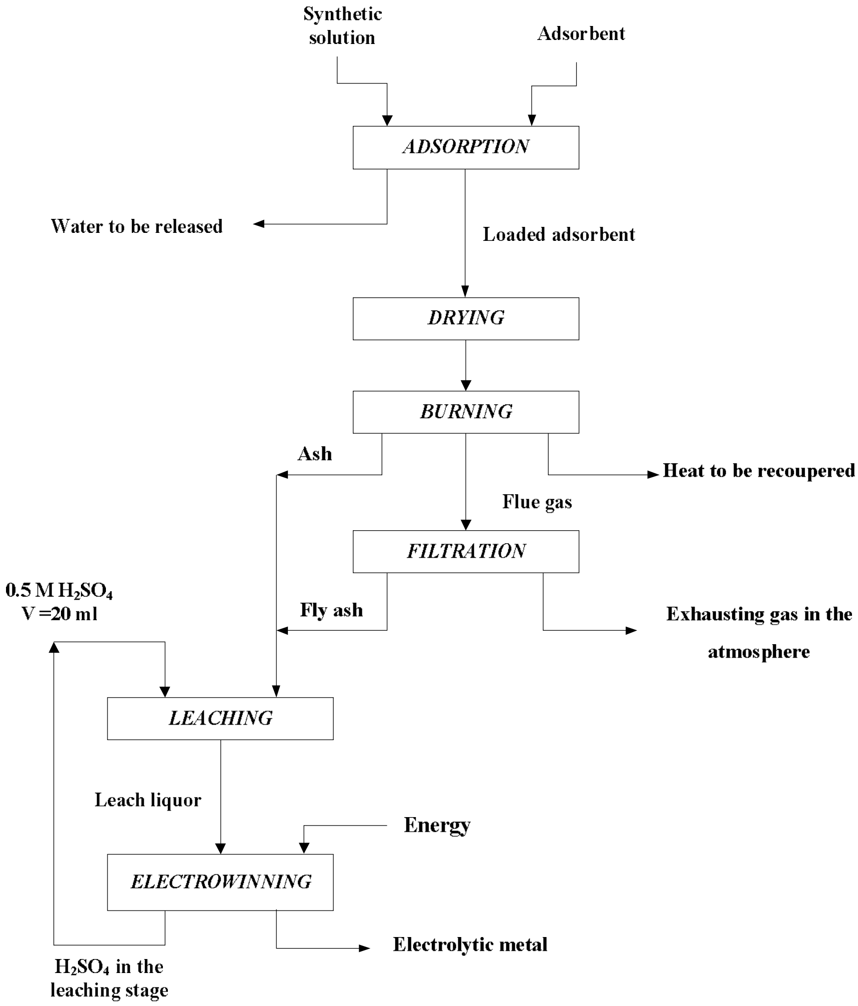

Fig. 4 Block diagram of the process for metal production from effluents by adsorption and electrowinning

Conclusion

Presented results showed that both adsorbents could be successfully used for the adsorption of copper from mine waters. Very high degree of adsorption could be achieved in column adsorption (> 99%) before the breakthrough point. Breakthrough curves allow us to evaluate the column capacity and to determine the breakthrough points for each of considered ions allowing a prediction of co-adsorption the other ions present in mine waters. The proposed process for metal removal and recovery from mine waters recommends the following: instead of stripping adsorbed metal by a proper desorption solution it is more suitable to burn the loaded adsorbent; to recuperate the produced heat; to leach the ash with a small volume of H_2SO_4 in which metal will be concentrated and to recover the metal by electrowinning.

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