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HEAVY METAL IONS ADSORPTION FROM MINE WATERS BY SAWDUST*

In this work the results on the batch and column adsorption of copper and some associated ions by employing linden and poplar sawdust as a low-cost adsorbent are presented. The mine water from a local abandoned copper mine, as well as synthetic solutions of those ions which are the main constituents of the mine water were both used as a model-system in this study. The adsorption ability of the chosen sawdust to adsorb heavy metal ions is considered as a function of the initial pH of the solution and kind of metal ions. At lower pH of solutions the adsorption percentage (AD %) decreases leading to a zero AD % at pH < 1.1. Maximum AD % is achieved at 3.5 < pH < 5. It was found that poplar and linden sawdust have both almost equal adsorption capacities against copper ions. The highest AD % (~80%) was achieved for Cu²⁺, while for Fe²⁺ it was slightly above 10%. The other considered ions (Zn²⁺ and Mn²⁺) were within this interval. The results obtained in the batch mode were verified through the column test by using the real mine water originating from an acid mine drainage (AMD) of the copper mine „Cerovo“, RTB Bor. The breakthrough curves are presented as a function of the aqueous phase volume passed through the column allowing having an insight into the column adsorption features. Breakthrough points were determined for copper, manganese and zinc ions. A very high adsorption degree - higher than 99% was achieved in these experiments for all mentioned ions. After completing the adsorption, instead of desorption, the loaded sawdust was drained, dried and burned; the copper bearing ash was then leached with a controlled volume of sulphuric acid solution to concentrate copper therein. The obtained leach solution had the concentration of copper higher than 15 g dm⁻³ and the amount of H₂SO₄ high enough to serve as a supporting electrolyte suitable to be treated by the electrowinning for recovery of copper. The technology process based on the column adsorption is proposed and discussed.

Key words: mine water; adsorption; leaching; sawdust.

There are many different industrial effluents containing heavy metal ions that at present significantly contribute to environmental pollution heavily polluting the surface - and underground waters [1-6]. The metal working industry, particularly electroplating and surface finishing plants, is an important sector producing enormous amounts of wastewaters containing mainly heavy metal ions but also, in some particular cases, noble metals that must be removed and recovered

from the exit streams prior to their releasing into the environment [1,2]. The second significant effluents producer is the electronic industry as well as recycling plants for spent electronic devices, containing various but, as a rule, very hazardous ions of heavy and noble metals (including platinum group of metals) in wastewaters arising from such factories [2]. Extractive metallurgy is also a huge polluter, heavily contaminating the surrounding soil and surface water streams with its wastewaters [1,3,4]. The industrial branches mentioned contaminate the environment with liquid effluents containing a relatively low concentration (up to several hundreds mg dm⁻³) of metal ions, among which the following metal ions predominantly appear: Cr, Ni, Zn, Cu, Zn, Pb and Cd.

Mine waters originating from active or closed copper mines (also known as “acid mine drainage” - AMD) are another extremely dangerous pollutants

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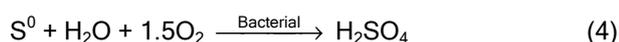
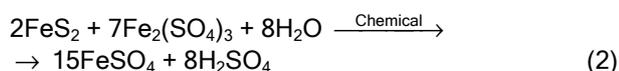
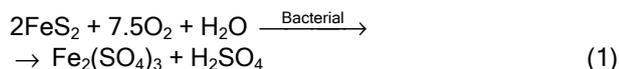
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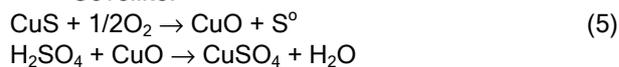
polluting their environment for a very long period of time [3-6]. They contain copper ions, sometimes in a considerable concentration ($\approx 1 \text{ g dm}^{-3}$), usually associated with an equivalent or even twice higher concentration of $\text{Fe}^{2+}/\text{Fe}^{3+}$, as a result of bacterial and chemical degradation of sulphide minerals from not excavated ore or from a gangue material deposited on dumps in the mine surrounding area. The presence of other heavy metal ions (Mn, Bi, Cd, Zn, Hg, Pb, Be, Ni, etc.) in mine waters depends on the mineralization of an ore body but their concentration is much lower than the concentration of copper or iron and does not exceed few mg dm^{-3} . Mine waters are as a rule acidic with the pH value mostly between 3 and 4 due to an elevated concentration of sulphuric acid contained in them, as a second product of bacterial oxidation of sulphide minerals. Pyrite is the most abundant mineral in poly-metallic sulphide ore deposits and in mining waste dumps. The oxidation of pyrite and copper minerals in an aqueous environment occurs *via* two simultaneous mechanisms, *i.e.*, biochemical involving bacteria and chemical way and can be described by the following stoichiometric reactions [4,6]:



The above reactions describe how acidity is generated and maintained in mine dumps.

Copper minerals in such dumps can also be decomposed either directly by a bacterial attack or by leaching with ferric ions formed through pyrite degradation (Eqs. (1) to (4)), which can be described by the following stoichiometric reactions [4,6]:

Covellite:



Chalcocite:



Elemental sulphur will be further oxidized as described by Eq. (4). Similarly like covellite, the oxidation of other present sulphides occurs by the same mechanisms releasing the other toxic metal ions into the solution. The ultimate result is a spontaneous mine water discharge in the form of AMDs, characterized by an elevated acidity and a considerably high concentration of metal ions associated with sulphate anions [3-6].

The flow-rate of the mine water spring varies over a wide interval, from a few litres to several cubic meters per minute and changes very much with seasons. So far, mine waters make serious, yet unresolved, environmental problems bringing metal ions and acid into the environment, heavily contaminating ground waters and soils in the vicinity of their origin [6-8].

The copper mine "Cerovo" is one of closed mines of the Copper Mining and Smelting Company Bor, located 11 km northern from the city of Bor, Serbia. Its production was ended in 2002 but this ex-mine still affects the quality of the surrounding creeks and rivers due to activities of its AMDs.

There are three AMDs flowing out from the outer lateral slope of the open pit dump, denoted in Table 1 as Spring 1, Spring 2 and Ecology Dam, having different concentrations of Cu^{2+} : in some cases a reasonably high ($> 1 \text{ g dm}^{-3}$), indicating a considerable content of residual copper minerals in the dump; in some others quite low ($< 0.2 \text{ g dm}^{-3}$). Surprisingly, a very low content of ferrous ions, not exceeding 10 mg dm^{-3} , is observed in all these AMDs, as shown in Table 1. Other heavy metal ions associated with the copper ones in these AMDs are present in amounts much higher than the maximum allowed concentration meaning that sulphide minerals of other heavy metal ions allied with copper are also present in the mine

Table 1. Average concentrations of heavy metal ions (mg dm^{-3}) in the AMDs from the closed copper mine "Cerovo" RTB Bor, Serbia

Metal	Spring 1	Spring 2	Ecology dam	MAC ^a
Mn	40.1	65.7	9.7	-
Cu	1050	1550	132.45	< 0.1
Fe	< 10	< 10	0.14	0.3-1
Ni	0.5	1.1	0.07	0.05-0.1
Co	2.1	5.6	0.32	0.2-2
Cd	0.2	0.4	0.05	0.005-0.01
Zn	> 20	> 27	5.7	0.2-1

^aMaximum allowed concentration according to the Regulation on hazardous substances in waters; Official Gazette of SRS, No 31(1982) p.1516

dump. Very low concentration of Fe^{2+} ($< 10 \text{ mg dm}^{-3}$) in the AMDs could mean a lack of pyrite and chalcopyrite in this dump.

The concentration of SO_4^{2-} was also high, $> 1200 \text{ mg dm}^{-3}$, according to the oxidation mechanism of the present minerals. The pH value is ≈ 3.4 , for Spring 1 and ≈ 3.6 for Spring 2, and the Ecology Dam. Mine waters from Spring 1 and 2, have a low flow-rate (few litres per minute) and flow now directly into surrounding creeks. Mine water from the Ecology Dam has a considerably lower concentration of copper ions than the other two springs but much higher flow-rate and consequently higher total metal ions content. This is why it was used to serve as a model-system in this study.

Due to the complexity of the problem associated with the metal removal and recovery from wastewaters (including AMDs), numerous technologies for their purification and the metal removal and recovery from such sources were considered in the past. Many of them are established and marketed, while some others are still under research and development. Up to now, there has been no economically sustainable and environmentally efficient technology for the elimination of heavy metal ions from wastewaters achieving a level low enough for their safe release into the environment. Wastewaters purification from heavy metal ions, particularly from copper ions as the most frequent pollutant, still attracts considerable attention of scientists dealing with the protection and conservation of our resources and ecosystem. Great efforts have been made in establishing a unique process for waste minimisation and the reclamation of metals from treated wastewater, thereby achieving a zero discharge of metal ions in the exit stream. Heavy metal ions can be removed from effluents, more or less effectively, by conventional technologies, such as: chemical precipitation, electrowinning or cementation. Precipitation produces sludge which must be disposed on a specially constructed dump and has to be further managed by a water mirror to prevent its dissipation as a dust to environment. Also, a spontaneous self leaching of formed metal hydroxides from the deposited sludge occurs due to acid rains what may be a potential risk to environmental pollution due to an accidental dump licking or overflowing. The electrowinning process can reduce copper ions concentration significantly [1,2,6], but it produces an elevated amount of sulphuric acid in the treated water as a by-product which must be neutralized by a proper neutralization reagent prior to its releasing into a natural recipient. It could be used if the treated wastewater can be recycled in the process. The cemen-

tation means a replacement of copper ion with some other less noble and less toxic metal but, however hazardous, it is freely released into a recipient. It also means a dissipation of the energy invested in producing of metal which has to be sacrificed in the cementation process.

Other technologies, comprising separation and concentration methods such as solvent extraction, adsorption or ion exchange, as well as reverse osmosis, electrodialysis or some other advanced membrane techniques combined with the electrowinning or precipitation techniques are also, in industrial use, a good way of selective removal of metal ions from wastewaters. Each of them also has its drawbacks which will not be considered here. Adsorption is a very convenient technique for the immobilization of ions onto adsorbent, particularly suitable for treating more dilute solutions containing often a few mg dm^{-3} of metal ions only. This technique, besides adsorption, comprises a stripping of metal ions from a loaded adsorbent by a proper stripping solution renewing adsorbent for the next adsorption cycle and further treatment of the bearing stripping solution making the whole technology more complex. In some cases, when the adsorbed metal is much worthier (precious metals) than the used adsorbent, as an alternative to the stripping stage is to burn the loaded adsorbent and to process the obtained ash for the recovery of a targeted metal. Activated carbon is a very effective adsorbent to adsorb hexavalent chromium, mercury ions, most noble metals and many others either in their simple ionic form or as organometallic complexes [9,10]. Various ion-exchange resins are also developed and marketed as an effective way for metal removal and the recovery from wastewaters and industrial effluents. Other more exotic but less expensive natural materials are at present under consideration for the adsorption of heavy metal ions, such as: peat [11,12], lignite, bentonite and clay [9,12], chitosan [13], lignocellulosic material [14], shell egg membrane [15], fly ash [16], marine algae and alginates [17-19,20] and many others.

Recently it was found that many by-products and waste materials from the foodstuff or agriculture, as well as from timber and wood industry, having a low price or even being no economically valuable, are able to adsorb metal ions to a certain extent. Materials that were tested as potentially possible low-cost sorbents were: walnut and nut shells [21,22], spent grains [23], olive stones [24], peanut skins, onion and orange peels, rice husks, leaves, coffee and tea waste [25, 26], tree fern [27] and other similar plant waste materials [28].

An interesting group of biosorbents are lignocellulosic or tannin rich waste materials such as wood bark and sawdust from various trees produced in large quantities in the timber industry and often making disposal problems. This group of natural materials has been very extensively considered to be employed as adsorbents for the adsorption of metal ions from wastewaters as shown in Table 2.

Sawdust, having a great potential as an adsorbent, has attracted the most attention of the scientists dealing with different aspects of wastewater purification by biosorption. If sawdust could be used as adsorbent, both the environment protection and wooden industry could benefit: effluent solutions containing heavy metal ions would be cleaned by a cheap adsorbent and a new market for sawdust and similar waste materials will be opened. Current researches have been performed with sawdust produced from different trees, mainly from local either coniferous or deciduous forests [22, 29-41], and some others more or less exotic trees depending on the country where the experiments were carried out. As for the aqueous phase, mainly synthetic solutions containing various ionic species (Ag^+ , Cd^{2+} , Co^{2+} , Cr^{3+} , Cr^{6+} , Cu^{2+} , Fe^{3+} , Mn^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} , Pd^{2+} , Pt^{4+} and Zn^{2+}), either alone or in mixture, were used as a model-system in testing the adsorption abilities of sawdust against some particular ions. It was pointed

out that metal ion adsorption depends essentially upon three main parameters: nature of sawdust, kind of heavy metal ions and the initial pH of solution.

Except for poplar, maple and oak sawdust [22,29-33,35], sawdust of other deciduous trees has seldom been used as adsorbents. No attention has hitherto been paid to the adsorption of heavy metal ions by linden and poplar sawdust - trees that are predominant in some forested areas of Balkan Peninsula. Beech sawdust was considered as an adsorbent for the adsorption of non-ionic pesticides [41], while modified beech bark was used as an adsorbent for heavy metal ions [42]. Not much attention has been paid so far to the mechanism of bonding of the metal ions onto sawdust. The researchers dealing with the sawdust adsorption supposed that an ion exchange mechanism between metal ions and some functional groups existing in the sawdust molecular structure was able to replace protons by some particular metal ion specie from the aqueous phase. Strong evidences to support this hypothesis have not been presented yet. In a few cases only [24,43,44], the authors assumed an exchange of earth-alkali and alkali metal ions from organic molecules with heavy metal ions from aqueous phase.

In spite of very extensive batch investigations of using low-cost adsorbents for heavy metal ions removal from the solutions which have been performed

Table 2. Summarized data about sawdust as adsorbent for heavy metal ions

Kind of sawdust	Ion	AD, %	q, mg/g	pH	Reference
MAPLE	Cu	90	-	4-8	Yu <i>et al.</i> [30]
Miscellaneous	Cu	/	2	4-7	Larous <i>et al.</i> [31]
Maple	Pb	90	-	3-7	Yu <i>et al.</i> [32]
Poplar	Cu	76.2	-	4	Sćiban <i>et al.</i> [33]
	Cd	31.9			
	Zn	37.5			
Mango	Cu	60	-	2-6	Ajmal <i>et al.</i> [34]
Poplar	Cu	90	-	4	Acar <i>et al.</i> [35]
Poplar and Fir	Cu	-	2.5 (poplar)	4	Sćiban <i>et al.</i> [29]
			2.2 (fir)		
	Zn	1 (poplar + fir)	6		
Miscellaneous	Cr	100	-	1	Gupta <i>et al.</i> [51]
Pinus Sylvestris	Cd	-	9	5.5	Costodes <i>et al.</i> [49]
	Pb	-	9		
Walnut	Pb	75	3.8	-	Yasemin and Zeki [39]
	Cd	60	3.3		
	Ni	33	1.7		
Neem	Cu	-	48.3	5	Srinivasa Rao <i>et al.</i> [40]
	Ni	-	31.5	4	
Notspecified	Cr(VI)	99.5	41.5	1	Gupta and Babu [51]
Maple	Ni	70	-	4	Shukla <i>et al.</i> [36]
Poplar, beech, linden	Cu	80	8	3.5-5.5	Božić <i>et al.</i> [44]

in the past two decades, not much attention has been paid to the column adsorption study by using the same materials [45-49].

This article presents the results of heavy metal ions adsorption by linden and poplar sawdust, from both synthetic solution containing single metal ionic specie and a real mine water having different metal ions in mixture. Both batch and column adsorption experiments were performed by the mentioned kinds of sawdust. Mine water originating from the closed copper mine "Cerovo" RTB Bor, Serbia was used through this study. The aim was to get an insight into the adsorption potential of the chosen sawdust for the adsorption of heavy metal ions, usually constituting AMDs and the parameters affecting the adsorption process.

EXPERIMENTAL

Adsorbate

Adsorption experiments have been carried in both batch and column mode. Batch experiments are described in detail earlier [44]. A series of these experiments were performed using synthetic, single ion solutions in order to determine the adsorption percentage, influence of the initial pH of solution as well as the sawdust selectivity against some particular ions.

Column experiments were carried out using both synthetic solution of copper and mine water from the Ecology Dam. This AMD was chosen because of its significantly lower concentration of copper and associated metals, as shown in Table 1, comparing to the other two springs. Synthetic stock solutions of Cu^{2+} , Zn^{2+} , Mn^{2+} and Fe^{2+} were separately prepared by dissolving the adequate sulphate salts of these metals having p.a. quality in distilled water to serve as artificial mono-ionic solutions having a constant initial concentration. From these solutions more diluted solutions were prepared if and when it was necessary.

Adsorbent

Linden and poplar sawdust, produced in local timber mills, were used as adsorbents in this study. The sawdust was sieved through a set of laboratory sieves and sieve fraction < 0.4 mm was used in the adsorption experiments. Specific surface area was determined for the used sieve fraction by employing the adsorption of methyl blue method [44,50] and using UV-visible spectrophotometer. The following values for the specific surface area were estimated:

Sawdust:	poplar	linden
Specific surface area ($\text{m}^2 \text{g}^{-1}$):	0.89	1.22

With the exception of sieving no other pre-treatment of sawdust has been made prior to the adsorption experiments.

Instrumentation

Concentration of considered heavy metal ions was determined by a Perkin-Elmer-403 atomic absorption spectrophotometer, while the pH was monitored by a WTW inoLab-720 pH-meter. Specific surface area of sawdust was evaluated from the absorbance data using Beckman DU-65 UV-visible spectrophotometer.

Experimental procedure

Batch adsorption experiments were performed in a series of beakers equipped with magnetic stirrers by stirring 1 g of the chosen sawdust with 50 ml of metal ion solution with known, previously determined, initial concentration of considered heavy metal ion and requested initial pH value. The suspension is agitated at 300 rpm for a known period of time ranging between 1 and 90 min. At the end of the predetermined interval of time the suspension was filtered by using laboratory filter paper (white label) and the aqueous phase was analysed on the remaining concentration of the metal. The final pH value for each interval was also measured. From the mass balance the amount of adsorbed metal ions was then calculated to get the adsorption capacity, defined as:

$$q(t) = \frac{c_i - c(t)}{m} V \quad (7)$$

where: $q(t)$ - mass of adsorbed metal per unit mass of adsorbent (mg g^{-1}); c_i and $c(t)$ are the initial and actual concentration of metal at time t ; V - volume of the treated solution (ml); m - mass of adsorbent (g).

The adsorption percentage as a function of time was also calculated from the experimental data by using the following relationship:

$$AD\% = 100 \left(1 - \frac{c(t)}{c_i} \right) \quad (8)$$

Adsorption column experiments were performed in a laboratory column (diameter 32 mm and 500 mm in height) filled with 50 g of sawdust forming a fixed bed therein the height of which was 30 cm. At the top and the bottom, a layer of glass wool was used serving as a calming section in the first case and as a bed support and a filter in the second one preventing particles to go out with the exit stream. The column was fed with metal bearing synthetic solution or mine water gravitationally, from a feeding reservoir positioned above the column. Passing through the bed in

a down-flow mode, the solution came out at the bottom. Water layer height above the sawdust fixed bed was kept constant in order to have an approximately constant flow-rate (10 ml min^{-1}) through the column. The column experiments were performed in a single-pass mode. The samples of the solution passed through the column were assayed periodically at a known volume of the solution passed through and analysed. From the mass balance, the adsorbed amount of metal ions was then calculated.

RESULTS

Effect of the initial pH of solution on the metal uptake by sawdust

In order to study how the initial pH influences the adsorption of copper ions onto sawdust, a series of adsorption experiments were performed by using a synthetic solution of copper ions as a model-system and varying the initial pH of solution from 0.8 to 5.3. The adjustment was made by adding sulphuric acid in the stock solution. The initial concentration of copper ions kept constant ($c_i = 0.2 \text{ g dm}^{-3}$) as well as the other process variables such as: stirring speed, concentration of sawdust ($c_{sd} = 20 \text{ g dm}^{-3}$), particles size ($d_p < 0.4 \text{ mm}$) and the process time that was 60 min - long enough to consider the system was equilibrated [44]. The results are shown in Fig. 1. It can be observed that the initial pH value greatly influences the adsorption percentage of copper ions. It increases with increasing the initial pH, from its zero value at the $\text{pH} < 1$ achieving its maximum in the pH range between 3.5 and 5. A slight decrease in the adsorption percentage at $\text{pH} > 5.5$ is due to the formation of soluble copper hydroxyl complexes and after that a copper hydroxide precipitate what was proven and elaborated extensively by Gaballah and Kilbertus [28] as well as by Ajmal *et al.* [34]. It has already been noticed that both kinds of sawdust used have almost the same capacity to adsorb copper [44] what has also been confirmed through the column experiments in the upcoming text.

A decrease of the adsorption capacity at lower pH is apparently due to a higher concentration of H^+ in the aqueous phase having an increased affinity to be easily adsorbed, which may compete with Me^{2+} for the adsorption sites in the sawdust internal structure. At $\text{pH} \leq 1$, where the adsorption degree has zero value, the presence of relatively high proton concentration may occupy almost all active sites obstructing the adsorption of heavy metal ions. Moreover, high H^+ concentration suppress the dissociation of some functional groups having the ability to dissociate and ex-

change their ions with metal ions from the solution. It was proven that the adsorption on sawdust occurs by an ion exchange mechanism when alkali and earth-alkali metal ions present in wooden molecular structure are replaced by metal ions or protons from the aqueous phase [43,44]. At higher pH, as the concentration of H^+ is being lower, the active sites are available for metal ions to be adsorbed. Moreover, the active sites may turn into dissociated forms and can exchange their alkali or alkali-earth ions from the adsorbent with heavy metal ions from the solution.

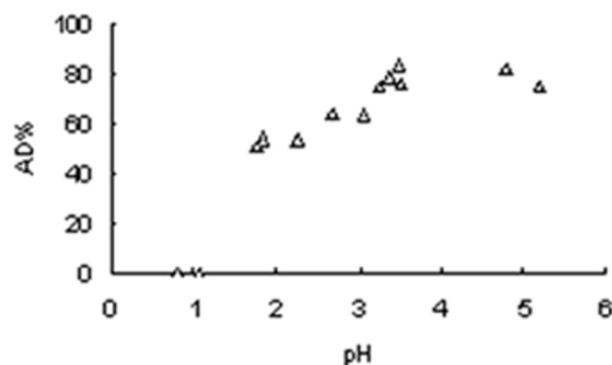


Figure 1. Change of the adsorption degree vs. initial pH of the aqueous phase: poplar sawdust, particles size $< 0.4 \text{ mm}$; $c_i = 0.2 \text{ g dm}^{-3}$; $c_{sd} = 20 \text{ g dm}^{-3}$.

From an engineering point of view, it is important to note that the adsorption of metal by sawdust is not convenient for more acid solutions due to competing of protons with metal ions to be adsorbed.

Adsorbability of considered ion species - selectivity of the process

From an engineering point of view, it is important to get evidence concerning the ability of sawdust to adsorb heavy metal ions expressed *via* adsorption percentage ($AD\%$) defined by Eq. (8), and to take out more data about the selectivity of the adsorbent against some particular ions. In Fig. 2 the curves on the adsorption percentage change vs. time for the considered metal ions are presented.

Obviously, the adsorption percentage curves increase sharply with time reaching, after 10 to 20 min, a steady state when the adsorption degree does not change any longer with time. The $AD\%$ at plateau values differs for different ions giving evidence about the maximum adsorption ability which can be achieved for each of the considered ionic species. According to Fig. 2, the highest adsorption percent is obtained for copper ions - where almost 80% is attained, while the adsorption of ferrous ions slightly exceeded 10%. It means that the used sawdust has reasonably

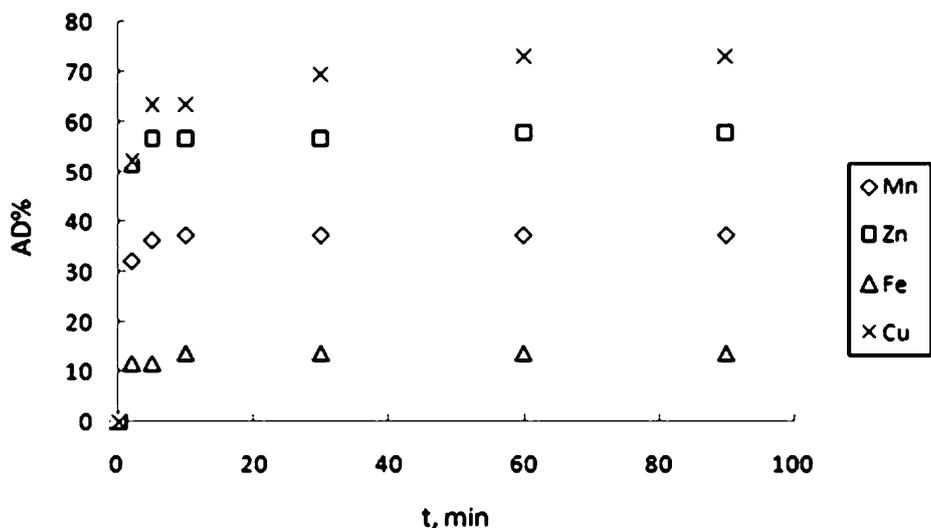


Figure 2. Adsorption percentage (AD %) against the process time: linden sawdust, particles size < 0.4 mm; $c_{sd} = 20 \text{ g dm}^{-3}$; $c_i = 50 \text{ mg dm}^{-3}$; $\text{pH}=5.01$.

poor adsorption ability against Fe^{2+} comparing to copper ions. It means that the sawdust used can adsorb copper ions selectively to the ferrous ions. Ranking the adsorption ability of sawdust, expressed *via* achieved AD% values of all here considered ions, the following series is obtained: $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Fe}^{2+}$.

The selectivity coefficient, defined as a ratio between the distribution coefficient of a targeted metal, $D_{\text{Me}^{2+}}$, and the distribution coefficient of Fe^{2+} , $D_{\text{Fe}^{2+}}$:

$$\beta = D_{\text{Me}^{2+}} / D_{\text{Fe}^{2+}} \quad (9)$$

for a constant pH, can give a useful evidence how many moles of a targeted metal ion will be immobilized on sawdust with one mole of ferrous ion in this case. The corresponding values of the selectivity coefficient, calculated over ferrous ions at a pH of 5, are:

$$\beta_{\text{Cu}^{2+} - \text{Fe}^{2+}} \approx 22; \beta_{\text{Zn}^{2+} - \text{Fe}^{2+}} \approx 11; \beta_{\text{Mn}^{2+} - \text{Fe}^{2+}} \approx 2$$

The adsorption kinetics

The adsorption kinetics was determined in the batch mode as described earlier by using single ion synthetic solutions of Fe^{2+} , Mn^{2+} , Zn^{2+} and Cu^{2+} . The results are presented in the linearized form in Fig. 3 by plotting the ratio $t/q(t)$ against the process time t , according to the Eq. (11). Many authors [10,11,24-26,40], dealing with the adsorption of ions on sawdust have found that the adsorption process follows a pseudo-second order kinetics what may be described by the following integral equation:

$$q(t) = \frac{q_e^2 k_a t}{(1 + q_e k_a t)} \quad (10)$$

Linearization of Eq. (10) leads to the following relationship:

$$\frac{t}{q(t)} = \frac{1}{k_a q_e^2} + \frac{t}{q_e} \quad (11)$$

where: $q(t)$ and q_e are the actual and equilibrium adsorption capacity of adsorbent (mmol g^{-1}), respectively; k_a is the adsorption rate constant ($\text{g mmol}^{-1} \text{min}^{-1}$); t is the process time (min). Plotting the left side of the Eq. (11) against process time gives straight lines for all considered ions here, as shown in Fig. 3, allowing the rate constants, k_a , and the equilibrium capacities, q_e , for the considered ions to evaluate, as presented in Table 3.

A very good fitting is achieved between the experimental results and the Eq. (11) confirming the second order kinetics of the adsorption. The regression coefficient has a value $R \approx 1$, as shown in Table 3, too.

Obviously, the fastest adsorption rate is achieved with ferrous ions while the Cu^{2+} adsorption has the smallest kinetics rate constant. Anyhow, this difference in kinetics is not as significant in the considered case as it is the equilibrium adsorption capacity as a measure of the adsorption ability of ions to be adsorbed and to what extent. Copper ions have the highest equilibrium adsorption capacity and ferrous ions the smallest one. The other two ions - Zn^{2+} and Mn^{2+} - have shown the modest adsorption ability.

Column adsorption study

To determine the adsorption capacity of sawdust under flow conditions, a series of column adsorption experiments were performed in down-flow mode, as

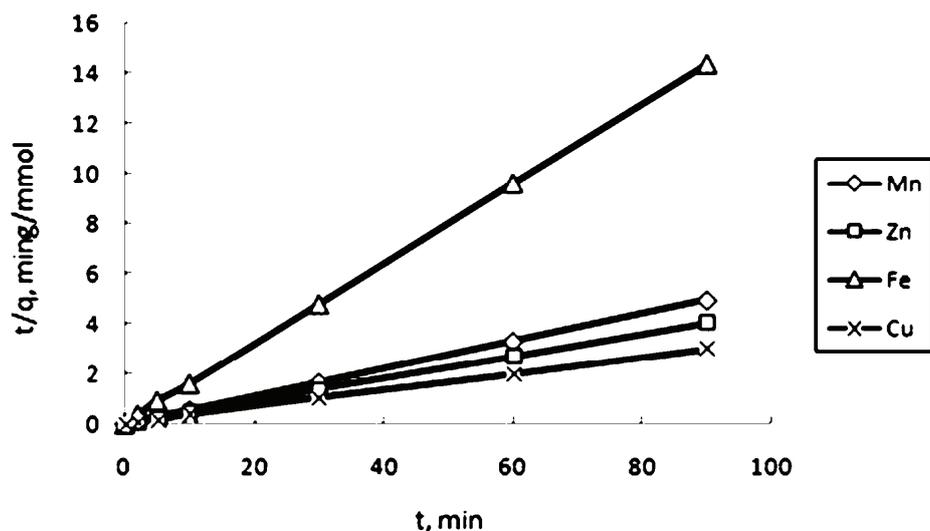


Figure 3. Linearization of the kinetic curves for: Δ - Fe^{2+} ; \square - Zn^{2+} ; \times - Cu^{2+} ; \diamond - Mn^{2+} linden sawdust; $c_{\text{sd}} = 20 \text{ g dm}^{-3}$; $\text{pH} = 5.01$; $c_i = 50 \text{ mg dm}^{-3}$.

Table 3. Rate constants, k_a , and the metal uptake, q_e , for the adsorption of the considered metal ions onto sawdust evaluated from Fig. 3

Parameter	Metal ion			
	Cu^{2+}	Fe^{2+}	Mn^{2+}	Zn^{2+}
$k_a / \text{g mol}^{-1} \text{ min}^{-1}$	1.3	90	19.82	7.34
$q_e \times 10^3 / \text{mmol g}^{-1}$	29.92	6.26	18.2	21.8
R^2	0.999	0.999	1	0.999

described in the Experimental part. Both synthetic copper sulphate solution and mine water from the Ecology Dam were used in this series of experiments. The results are presented in the form of breakthrough curves by plotting a normalized concentration d/c_0 , (a ratio of an actual outlet concentration at a volume passed through the bed, c , and the initial concentration in the feeding solution, c_0) against the volume of the solution passed through the column, V , as is presented in Fig. 4 for both used sawdust and for the synthetic solution containing copper ions only.

At the very beginning of the column adsorption process, the feeding solution flowing into the column passes through a virgin bed and the top layers of sawdust presents the adsorption zone (part of the bed where the adsorption occurs) and will be first saturated by the adsorbed metal ions. The exit stream, leaving the column from the bottom, will be completely liberated from metal ions so that in the first few issued samples the concentration of metal ions is below the detectable concentration of the analysing device and may be consider to have a zero value. As

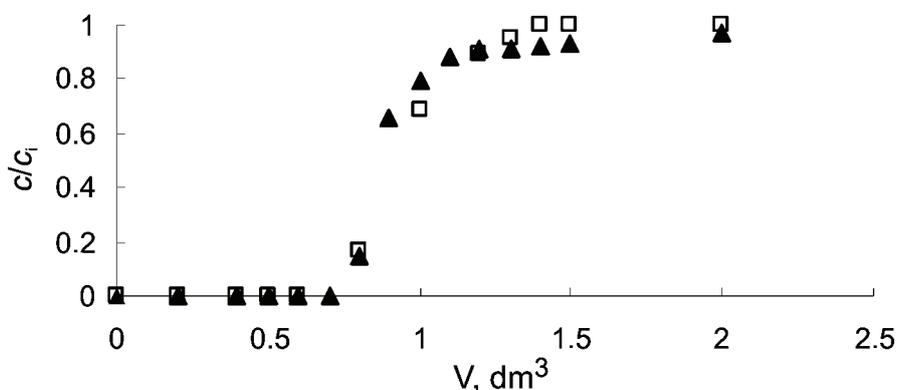


Figure 4. Normalised copper concentration plots against the volume passed through the column: \square - Poplar sawdust; \blacktriangle - Linden sawdust; bed height 30 cm; initial concentration of $\text{Cu}^{2+} = 200 \text{ mg dm}^{-3}$; flow rate = 10 ml min^{-1} .

the volume of the solution passed through the column increases, the adsorption zone will be shifted continuously downwards the bed where the sawdust is not saturated yet approaching the column bottom what will result in the appearance of considered ions in the exit stream. The detection of metal ions in that issued sample is an indicator that the adsorption zone reached the column bottom. This moment is known as the breakthrough point on the curve and the corresponding volume is the breakthrough volume, V_b . Continuing the adsorption process leads to an increase in the metal ion concentration in the following issued samples and consequently to a sharp increase of the normalized concentration with the volume on the graph approaching to the unity. When the concentration of ions in the inlet and the outlet stream gets equal, the entire bed is fully loaded and equilibrated with the feeding solution and the adsorption is completed, as shown in Fig. 4, where the breakthrough curves for linden and poplar sawdust are presented. Beside a very good curves shape obtained for both kinds of sawdust, Fig. 4 illustrates that both kinds of sawdust have an equal capability to adsorb copper ions. The breakthrough points appear at the same volume for both used sawdust.

From an engineering point of view, determination of the breakthrough curve allows the adsorption capacity of a column to evaluate. Usually, in an engineering calculation, the breakthrough point is placed at $d/c_0 = 0.5$, but sometimes at $d/c_0 = 0.1$, depending on the targeted concentration of a metal ion in the outlet stream. In the considered case, using $d/c_0 = 0.5$ as the breakthrough point and the volume corresponding to this value, $V_b = 0.75 \text{ dm}^3$, the computed adsorption capacity of the column is: $q = 1.5 \text{ mg g}^{-1}$ which means that the bed is not saturated yet and this

value is far from that one given in Table 3, as an equilibrium adsorption capacity. A sharp slope on the linear part of the breakthrough curve indicates that the bed will get saturated very quickly.

From a pragmatic point of view, it is more important to see how the inlet concentration of considered ions in mine water will change passing through the adsorption column. Working with mine water from the Ecology Dam, the collected samples were analysed on Cu^{2+} , Mn^{2+} and Zn^{2+} as those ions the concentration of which is much higher than the concentration of other ions presented in the mine water (see Table 1). The comparison with the results obtained when the adsorption was performed by using synthetic copper solution with an initial concentration of 0.2 g dm^{-3} and constant initial pH of 5.01 was made. In both cases the flow rate and mass of sawdust were kept constant. The results are presented in Fig. 5 by plotting the normalised concentration change of Cu^{2+} against the volume of water passed through the column. The shape of both breakthrough curves is almost the same indicating that the adsorption rate is equal in both cases. However, the mine water breakthrough curve is shifted slightly towards a lower breakthrough volumes and the appearance of the breakthrough point occurred earlier than in case of the synthetic solution. It means that the adsorption capacity of sawdust, calculated on copper, is slightly reduced. In mine waters, as shown in Table 1, besides copper ions as a predominant specie there are also many other heavy metal ions (Mn^{2+} and Zn^{2+} , before all, with a concentration higher than the other ions), which may affect the adsorption of copper ions. As one can see from Table 3, the kinetics of the adsorption of both Zn^{2+} and Mn^{2+} is reasonably faster (approximately 5 and 15 times, respectively) comparing to the kinetics of copper ions ad-

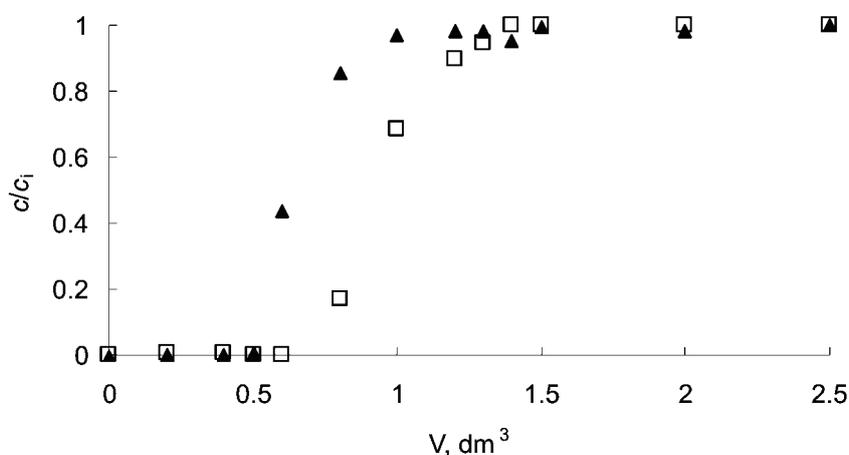


Figure 5. Normalised concentration plots against the volume passed through the fixed bed column: \square - synthetic solution ($\text{Cu} = 0.2 \text{ g dm}^{-3}$); \blacktriangle - mine water ($\text{Cu} = 0.135 \text{ g dm}^{-3}$); bed height 30 cm (50 g); poplar sawdust, particles size $< 0.4 \text{ mm}$; flow rate 10 ml min^{-1} .

sorption so that one should expect, based on our earlier results [44], a co-adsorption of these ions. The earlier appearance of the Cu^{2+} breakthrough point on the mine water breakthrough curve could be considered, most probably, as a consequence of a simultaneous adsorption of the other divalent heavy metal ions and protons present in the mine water, which compete with copper ions for the active sites on sawdust particles. Therefore, the adsorption capacity of sawdust to adsorb copper ions is slightly reduced.

To check this assumption, the change of Mn^{2+} and Zn^{2+} concentrations were also monitored during the column adsorption of copper ions and plotted in the normalized form against the volume passed through the column, together with the copper ion concentration. The breakthrough curves of all three considered ionic species are presented in Fig. 6.

As one can see, the breakthrough point of manganese ions appears first because of its lower adsorption percentage and smaller adsorption capacity

which does not exceed 1 mg/g of sawdust [44]. The breakthrough curve is very steep and quickly after the breakpoint the adsorption of manganese ion does not occur anymore. The breakthrough points for both zinc and copper ions are shifted towards higher volume values, almost twice higher than the V_b of manganese ion is. Both ion species have higher adsorption capacities than Mn^{2+} [44] and higher adsorption percentage. The breakthrough points of Zn^{2+} and Cu^{2+} are close each other meaning that the ability of these species to be adsorbed is almost equal, what is in accordance with the adsorption degree vs. time curves, presented in Fig. 2.

It was observed and discussed by Božić *et al.* [44] that the initial pH changes during the adsorption. When measuring the pH of assayed samples in the column adsorption process a certain increase in the solution pH with the volume passing through the column was also noticed, as presented in Fig. 7.

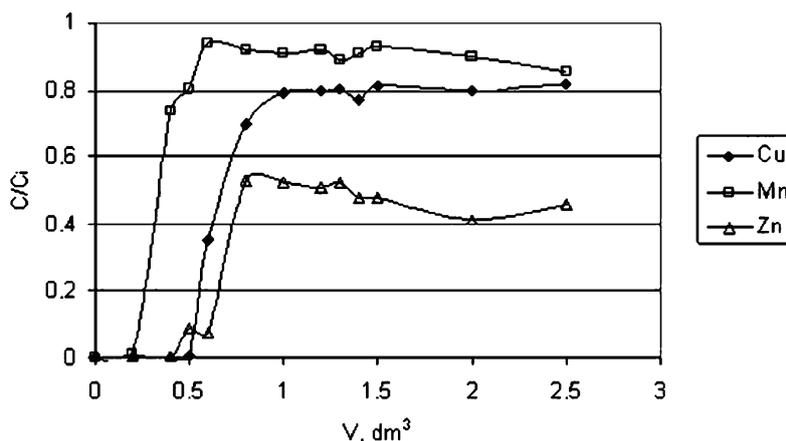


Figure 6. Normalised concentration plots against the mine water volume passed through the fixed bed column: \square - Mn^{2+} ; \blacklozenge - Cu^{2+} ; \triangle - Zn^{2+} ; bed height 30 cm; Poplar sawdust, particles size < 0.4 mm; flow rate 10 ml min^{-1} .

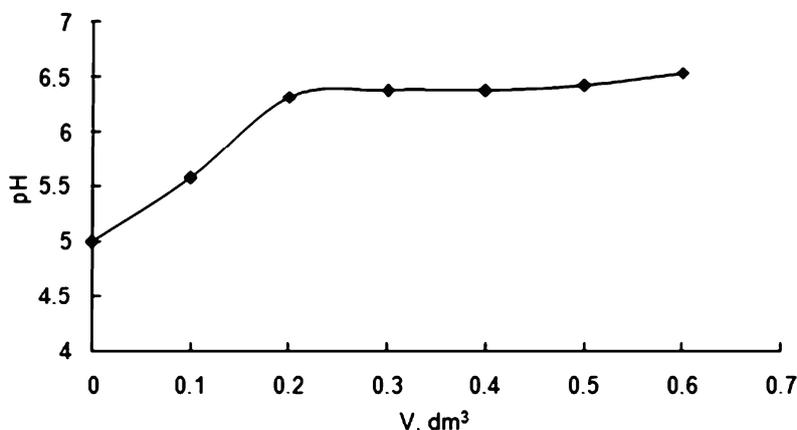


Figure 7. Change of the initial pH of solution with the volume passed through the column Poplar sawdust, particles size < 0.4 mm; flow rate 10 ml min^{-1} ; Bed height 30 cm; $\text{Cu} = 0.2 \text{ g dm}^{-3}$.

The pH increase means a co-adsorption of protons with metal ions. This effect causes an equivalent decrease in sawdust adsorption capacity which is a bad aspect of the process. A positive aspect is that sawdust, adsorbing H^+ , affects the wastewater acidity decreasing a consumption of an agent which has to be spent in the neutralisation process that should follow the adsorption step, if the complete treatment of mine waters occurs, prior to its releasing into a natural recipient.

Process technology for metal ion removal and recovery from mine waters

Not much attention has been paid so far in the relevant literature to the stripping of adsorbed metals from loaded sawdust. In few cases only, desorption has rather been mentioned than studied extensively [24,30,32,34]. The achieved desorption degree, in the mentioned references, was rather modest and did not exceed 50% of the metal amount adsorbed by saw-

dust. Further treatment of sawdust, comprising washing out the stripping solution from sawdust renewing it for the next adsorption cycle has not been considered at all by anyone discussing a desorption stage.

Using “low-cost” adsorbents like sawdust, the question is always what is more convenient and economically sustainable:

- to regenerate and renew the loaded sawdust by desorption using a proper desorption agent;
- or to destroy the loaded sawdust burning it in order to produce heat and to recover a metal content from the produced ash.

Starting from the position that sawdust is a cheap material, not quite suitable for recycling - we have considered and experimentally checked the second way as a possible process route for metal removal and recovery from loaded sawdust. Block diagram of the process for copper bearing mine waters treatment is presented in Fig. 8.

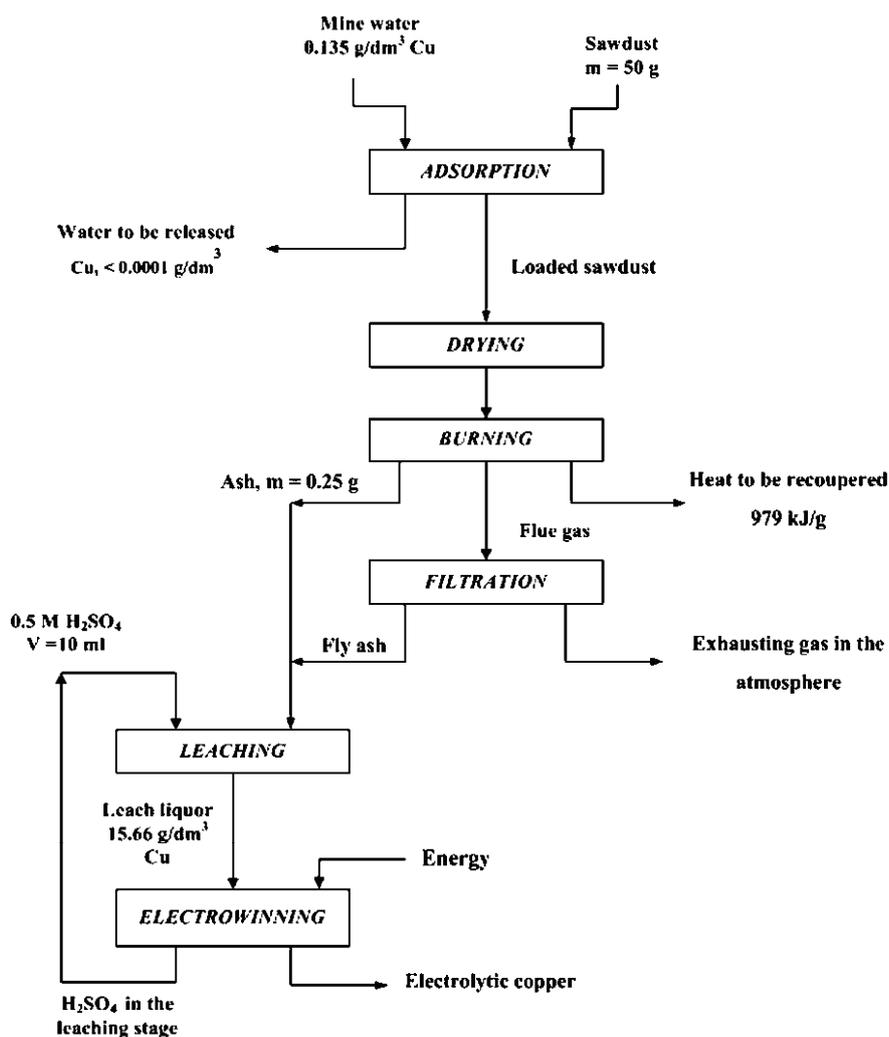


Figure 8. Block diagram of the process for copper recovery from mine waters and similar sources by adsorption and electrowinning.

It comprises the following: After completing the column adsorption, instead of desorption, the loaded sawdust was drained, dried and burned concentrating the metal content in the produced ash; the collected copper bearing ash was then leached with a small volume of sulphuric acid solution to concentrate copper and other metals therein. In such a way, the obtained leach solution had a concentration of copper ions $c_L > 15 \text{ g dm}^{-3}$, what is more than two order of magnitude higher than the concentration in the feeding solution (0.135 g dm^{-3}). The concentration of copper ions in the leach solution is suitable to be further treated by the electrowinning in order to recover copper in this case and, in principle, some other valuable metal from the leach solution [2,6]. The heat energy released by burning the sawdust may be recuperated and used for heating or steam production. The proposed process could be particularly suitable, besides mine waters treatment, for other similar solutions originating from extractive metallurgy of copper as well as for rinse waters from metal working and electroplating plants.

CONCLUSIONS

Through this study, essential data were collected for an engineering approach in design of the adsorption process using sawdust as a low-cost adsorbent. Sawdust of deciduous trees like linden and poplar considered in this study appears to be a promising adsorbent for the efficient removal of copper ions but is also, to a less extent, suitable for the other heavy metal ions removal from weakly acid sources like mine waters, rinse waters and other similar effluents containing in a small quantity heavy metal ions. The adsorption of heavy metal ions strongly depends on the process time, the initial pH of the aqueous phase and kind of ions to be adsorbed. The adsorption process is fast and after ten to twenty minutes of contact time, the system is equilibrated. Maximum adsorption degree is achieved in the pH range between 4 and 5.5. Acidifying the aqueous phase leads to a decrease in the adsorption capacity of sawdust. The adsorption of metal ions is terminated at pH close to unity. The highest adsorption degree is obtained for copper ions where almost 80% is achieved, while the adsorption of ferrous ions slightly goes above 10%. Ranking the ability of the considered ions to be adsorbed on sawdust, the following series is obtained: $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Fe}^{2+}$. The used sawdust has shown certain selectivity in the adsorption of heavy metal ions. Calculated selectivity coefficients over ferrous ions are:

$$\beta_{\text{Cu}^{2+}}^{\text{Fe}^{2+}} \approx 22; \beta_{\text{Zn}^{2+}}^{\text{Fe}^{2+}} \approx 11; \beta_{\text{Mn}^{2+}}^{\text{Fe}^{2+}} \approx 2$$

Through fixed bed column experiments, the adsorption of copper was tested using both synthetic single ion solution and mine water containing a mixture of various ions, with copper as prevailing ionic specie. Very high degree of copper ions adsorption was achieved in the column adsorption ($> 99.7\%$) before the breakthrough point. Both kinds of sawdust used have an equal ability to adsorb copper ions. The pH of solution increases slightly during the adsorption meaning a co-adsorption of protons contained in a treated solution.

The process for mine water treatment is proposed and experimentally proven. The proposed process for metal ions removal and recovery from mine waters consists of the following: instead of a desorption step by employing a proper desorption solution it is more suitable to burn the loaded sawdust, recuperate the produced heat energy, leach the collected ash in which targeted metal is concentrated and to recover it by the electrowinning process that can support the whole process economy.

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