Adsorption of heavy metal ions by sawdust of deciduous trees

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ABSTRACT

The adsorption of heavy metal ions from synthetic solutions was performed using sawdust of beech, linden and poplar trees. The adsorption depends on the process time, pH of the solution, type of ions, initial concentration of metals and the sawdust concentration in suspension. The kinetics of adsorption was relatively fast, reaching equilibrium for less than 20 min. The adsorption equilibrium follows Langmuir adsorption model. The ion exchange mechanism was confirmed assuming that the alkali-earth metals from the adsorbent are substituted by heavy metal ions and protons. On lowering the initial pH, the adsorption capacity decreased, achieving a zero value at a pH close to unity. The maximum adsorption capacity (7–$8\,\mathrm{mg\,g^{-1}}$ of sawdust) was achieved at a pH between 3.5 and 5 for all the studied kinds of sawdust. The initial concentration of the adsorbate and the concentration of sawdust strongly affect the process. No influence of particles size was evidenced. A degree of adsorption higher than 80% can be achieved for Cu^{2+} ions but it is very low for Fe^{2+} ions, not exceeding 10%.

1. Introduction

There are many different industrial streams containing heavy metals that at present significantly contribute to environmental pollution. The metal working industry, particularly electroplating and surface finishing of metals, is an important sector producing enormous amounts of wastewaters containing mainly Cu^{2+}, Ni^{2+}, Zn^{2+}, Sn^{2+}, CrO_4^- ions, but, less frequently, also some other metals. The second significant effluent producer is the electronics industry, as well as the recycling industry of spent electronic devices, with various but very hazardous effluents containing in addition to the already mentioned, also ions of noble metals as well as the rare and platinum group of metals in the wastewaters from the electronics plants. Extractive metallurgy is also a paramount polluter, damaging heavily soil and surface water streams and emitting heavy metals into the surroundings. These industrial branches contaminate the environment with liquid effluents containing a relatively low concentration (up to several hundreds $\mathrm{mg\,dm^{-3}}$) of metal ions, among which the following metals: Cr, Ni, Zn, Cu, Zn, Pb and Cd are, as a rule, the most abundant ones.

Mine waters originating from active or closed copper mines contain copper ions, sometimes in a considerable concentration ($\approx 1\,\mathrm{g\,dm^{-3}}$), usually associated with an equivalent or even twice higher concentration of Fe^{2+}/Fe^{3+} ions, as the outcome of bacterial degradation of copper and iron sulphide minerals. The presence of other heavy metals (Mn, Bi, Cd, Zn, Hg, Pb, Be, Ni, etc.) in these waters depends on the mineralization of the ore body but their concentrations are much lower than the concentration of copper or iron and do not exceed several $\mathrm{mg\,dm^{-3}}$. Mine waters are, as a rule acidic, having a pH value mainly between 3 and 4 due to an elevated concentration of sulphuric acid contained in them, also as a product of bacterial oxidation of sulphide sulphur. The volume of mine water springs varies over a wide interval—from a few litres to several cubic meters per minute, and changes considerably with season. Nevertheless, mine waters constitute a serious, unresolved problem to environment, transporting metal ions and acid to the surroundings and damaging heavily ground waters and soil [1–3].

Due to the complexity of the problems associated with metal removal and recovery from wastewaters, numerous techniques are available for water purification and metal removal and recovery from wastewaters. Many of them are established and marketed, while some others are under development or still in the experimental stage. To date, there is no efficient technology for the elimination of heavy metals from wastewaters which achieves a level low enough for their safe release into the environment. Wastewaters purification from heavy metals, as the most hazardous pollutants, still attracts considerable attention of scientists dealing with the protection and conservation of our resources and ecosystem. Great efforts have been made and still being made to establish a unique process for waste minimization and the reclamation of metals from treated wastewater, thereby achieving a zero level of metal ions in the exit stream. Damaging heavy metal ions can be removed from effluent solutions, more or less effectively, by conventional technologies, such as, for example, chemical precipitation,

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electrowinning or cementation of the ions present in wastewater by a less noble metal. 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 are also in industrial use as a way of selective removal and concentration of metal ions from waste streams.

Sorption methods are particularly convenient to immobilize ions onto a solid phase surface, particularly from very dilute solutions such as wastewaters, containing frequently only a few mg dm^{-3} of ions. Activated carbon is effective to adsorb hexavalent chromium, mercury, most noble metals and many others either in their simple ionic form or complexed by organic ligands [2,4,5]. Also, various ion exchange resins have been developed and marketed for the effective removal and recovery of metals from solutions. Other more exotic but less expensive natural materials are also under consideration for the adsorption of heavy metals, such as peat [6,7], lignite, bentonite and clay [3,7], chitosan [8], lignocellulosic material [9], shell egg membrane [10], fly ash [11], marine algae and alginates [13–17], dead biomass [16] and many others. The biosorption of heavy metals from aqueous solutions is a relatively new approach, still under research and development, for the industrial treatment of wastewaters. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to a very low level and the use of inexpensive materials as sorbents. Biosorption processes are particularly suitable for the treatment of wastewater streams containing more dilute solutions of heavy metals, or when a very low concentration of heavy metals is required in an exit stream prior to its releasing into a recipient.

A great interest has recently been directed to the biosorption of heavy metals from solutions using different bio-materials as adsorbents. Extensive research in the past decade showed that many agricultural by-products and waste materials from the foodstuff industry, having a low price or even no economic value, 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 [16,18 and literature cited therein], spent grain [19], olive stones [20], peanut skins, onion and orange peels, rice husks, leaves, coffee and tea waste [21,22], tree fern [23] and other similar plant waste materials [24]. Another large 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 posing disposal problems, have been considered for employment as adsorbents for the adsorption of different, but mainly hazardous, metal ions from wastewaters. Sawdust, having a great potential as an adsorbent, has attracted the most attention of scientists dealing with different aspects of wastewater purification by biosorption. If sawdust could be used as an absorbent, both environment protection and wood 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 research has been performed with sawdust produced from different kind of trees, mainly from local either coniferous or deciduous forests [18,25–37], such as: oak and fir [18,25,29], mango [30], poplar [25,29,31], maple [26,32,33], pine [18,34], walnut [18,36], and some others more or less exotic trees depending on the country where the experiments were realised. As 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, served as model-systems in the testing the adsorption abilities of sawdust. It was pointed out that metal adsorption depends essentially upon three main parameters: the nature of sawdust and its pre-treatment, the kind of heavy metal ions and the pH of the solution.

Except for poplar, maple and oak sawdust [18,25–29,31], the sawdust of other deciduous trees have seldom been used as adsorbents. No attention has hitherto been paid to the adsorption of heavy metals by linden and beech sawdust. Beech sawdust was considered as an adsorbent for the adsorption of non-ionic pesticides [37], while modified beech bark was used as an adsorbent for heavy metals [38]. Also, no much attention has been paid to the pH behaviour during the adsorption and its role in the process mechanism. With a few exceptions [20,40], there are rather speculations and assumptions but no strong evidences about the ion exchange mechanism in the relevant literature.

This study presents the results of heavy metal ions adsorption by linden, poplar and beech sawdust, provided from local timber mills, from synthetic solutions containing single ionic species, *i.e.*, Cu, Zn, Ni, Cd, Mn and Fe. These trees are predominant in some forest areas on the Balkan Peninsula, particularly in those parts where active or closed base metals mines already exist. They are the main source in the wood industry and their sawdust could be a good candidate as potential low-cost adsorbent for heavy metals. The aim of this study was to obtain an insight into the adsorption potential of the chosen kinds of sawdust for the adsorption of heavy metal ions, usually constituting acid mine drainages, and the parameters affecting the adsorption process. The aim also is to consider the adsorption kinetics and the equilibrium state and parameters affecting it as well as to study the behaviour of the pH of solution during the process and its influence on the metal adsorption and the mechanism of bonding. Through this study, essential kinetics and thermodynamic data are evaluated making a good base for an engineering consideration of the column adsorption of heavy metals by sawdust from real solutions.

2. Experimental

Adsorption experiments of the following heavy metal ions: Cu, Zn, Mn, Cd, Fe and Ni onto sawdust were performed from synthetic solutions. These metals appear most frequently in the acid mine drainages of active or closed copper mines, adding significantly to the pollution of surface water streams and soil.

2.1. Absorbent

Sawdust of linden (*Tilia*), poplar (*Samsun Clone*) and beech (*Fagus Sylvatica*), produced in a local timber work shop, were used as adsorbents in this study. Each kind of sawdust was sieved through a set of laboratory sieves and four sieve fractions were chosen for employment in the adsorption experiments: ($-1 + 0.8$ mm), ($-0.8 + 0.63$ mm), ($-0.63 + 0.4$ mm) and ($-0.4 + 0$ mm). The specific surface area was determined only for the finest used sieve fraction by the adsorption of Methyl Blue method [39], using a UV–visible spectrophotometer and the following values were obtained:

Sawdust	Beech	Poplar	Linden
Specific surface area (m^2 g^{-1})	1.08	0.89	1.22

With the exception of sieving, the sawdusts were not pre-treated prior to the adsorption experiments.

2.2. Chemicals

Stock solutions of the chosen Me^{2+} ions were prepared by dissolving the corresponding sulphate salts of the metals (Analytical Grade–Merck) in distilled water in an amount to obtain an initial concentration $C_i = 0.2$ g dm^{-3}. Lower concentrations were then prepared when required by further dilution of the stock solution with distilled water. Sulphuric acid was used for pH adjustment when the effect of this variable was investigated.

2.3. Instrumentation

The concentrations of the considered heavy metals were determined using a PerkinElmer-403 atomic adsorption spectrophotometer, while the pH was measured by a WTW inoLab-720 pH-meter. The specific surface area was evaluated from absorbance data obtained using a Beckman DU-65 UV–visible spectrophotometer.

2.4. Experimental procedure

The adsorption experiments were performed in a batch mode 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 a known, previously determined, initial concentration of the considered heavy metal ion and the required initial pH value. The suspension was agitated at 300 rpm for a known period of time, ranging between 1 and 90 min. At the end of the predetermined time, the suspension was filtered and the remaining concentration of metal in the aqueous phase was determined. The final pH value was also measured. From the mass balance, the amount of adsorbed metal was then calculated to obtain the adsorption capacity, defined as:

$$q(t) = \frac{((C_i - C(t)) * V)}{m} \tag{1}$$

where $q(t)$ is the mass of adsorbed metal per unit mass of adsorbent (mg g^{-1}); C_i and $C(t)$ are the initial and actual concentration (g dm^{-3}) of metal at time t, respectively; V is the volume of the treated solution (ml); m is the mass of adsorbent (g).

The adsorption degree, AD, as a function of time was also determined from the experimental data using the following relationship:

$$AD\% = \left(1 - \frac{C(t)}{C_i}\right) \times 100. \tag{2}$$

Based on the adsorption kinetics experiments, the process time for the equilibrium adsorption experiments was chosen, long enough assuming that the considered sorbent/sorbate system is equilibrated. The following parameters of the process were changed during these experiments: kind and amount of sawdust; the particles size; the initial pH of the solutions and the initial concentration of the considered ions. All experiments were performed at ambient temperature.

3. Results and discussion

3.1. Adsorption kinetics

The adsorption kinetics were investigated with an aim of obtaining a deeper insight into how the amount of adsorbed metal changes with time and about the process time required—to achieve equilibrium between the aqueous and the solid phase for a given combination of sawdust and the to be adsorbed metal ions. In this series of experiments, the initial concentration of metal ions was approximately 50 mg dm^{-3} and the initial pH had a value around 5. The exact pH value for each metal solution was measured before the experiment and its change was monitored during the experiments. To avoid any influence of other foreign cations on the adsorption, no buffer for adjusting the pH was added in the treated solution. Based on the preliminary experiments, the process time was chosen to be 90 min in this series of experiments. The metal uptake against time is presented in Fig. 1 for all the investigated ions.

From the graphs given in Fig. 1 (left column), it seems as if the process occurred in two steps. Within the first 5–10 min, the adsorption occurred rapidly, coming in a steady state after about 30 min, after which no remarkable increase in $q(t)$ was observed.

The sudden increase of $q(t)$ at the very beginning of the process is attributed to an abundant availability of active sites on internal and external surface area of the adsorbent. With the progressive occupancy of these sites by metal ions, the process comes into a period of slower adsorption, during which the less accessible sites are occupied by metal ions. Mostly, metal adsorption occurs in the first 20 min. A similar shape of curves as those presented in Fig. 1, was reported by the other scientists dealing with metal adsorption on various low-cost adsorbents [27,28,31]. The adsorption kinetics of metals on sawdust may be considered as a pseudo-second order reaction, as reported by several authors [5,6,20,21,23,36].

The adsorption rate can be described by the following differential equation:

$$\frac{dq(t)}{dt} = k_a[q_e - q(t)]^2 \tag{3}$$

Assuming the initial condition $q(t) = 0$ for $t = 0$, the following integral form of Eq. (3) is obtained:

$$q(t) = \frac{q_e^2 k_a t}{1 + q_e k_a t} \tag{4}$$

where q_e is the mass of adsorbed metal per unit mass of adsorbent (mg g^{-1}) at equilibrium; k_a is the adsorption rate constant (g mg^{-1} min^{-1}).

Rearranging Eq. (4) leads to its linear form:

$$\frac{t}{q(t)} = \frac{1}{k_a q_e{}^2} + \frac{t}{q_e} \tag{5}$$

Introducing the experimental data into Eq. (5) and plotting $t/q(t)$ against the process time gives a straight line for each of the considered metals. These plots are also presented in Fig. 1 (right column), showing a very good fit with the assumed pseudo-second order model. From the slopes of the graphs presented in the right column of Fig. 1, the equilibrium metal uptake (q_e) for a given initial concentration of each ion is determined, while from the intercepts the adsorption rate constants k_a were evaluated and given in Table 1. The regression coefficients are also given in Table 1. As can be seen, they are close to unity for all the considered metals, confirming the good fit of the experimental results with the considered second order kinetics model of adsorption.

3.2. Change of pH with time

Measuring simultaneously the pH value of the aqueous phase during the adsorption of metal ions a certain slight change has been remarked with time as is depicted in Fig. 2(a and b).

This change is particularly remarkable at the very beginning of the process corresponding to the period of the fastest increase in $q(t)$. These only small changes indicate the complexity of the mechanism of bonding. Most authors considering the mechanism of adsorption have adopted the model of active sites existing in the cellulose structure of sawdust and an ion exchange mechanism of adsorption [20,25,27–29,35,36,40,41]. These active sites containing lignin, tannin or other compounds with phenol groups in their molecules are able to replace protons with metal ions accordingly to the stoichiometric reaction:

$$Me^{2+} + 2(-ROH) = Me(-RO)_2 + 2H^+ \tag{6}$$
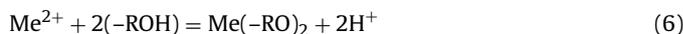
Replacing protons from donors constituting the active sites in the wood structure by metal ions should affect an instantaneous decrease in the pH of the aqueous phase. Such an approach could be considered as satisfactory for Cu^{2+} and Cd^{2+} ions, where a sudden drop of pH was observed in the first few minutes of the process when the highest increment of the adsorption capacity was observed (see Fig. 2a). After the initial period of decreasing, the pH slowly increased, achieving a constant value when the adsorption
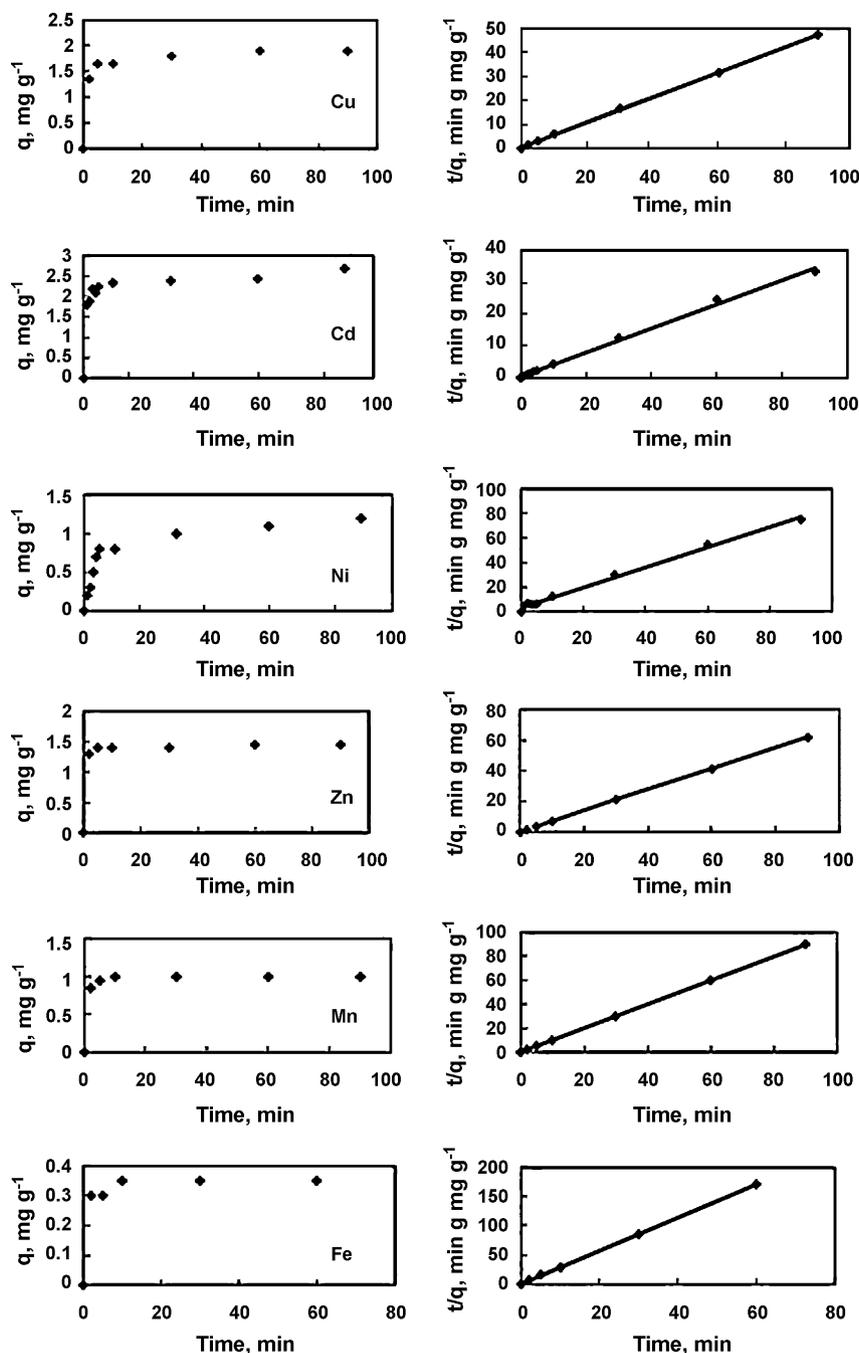
Fig. 1. Change of the adsorption capacity with process time for different metals: linden sawdust particle size < 0.4 mm; $C_{sd} = 20\,\mathrm{g\,dm^{-3}}$; initial metal concentration $C_i = 0.05\,\mathrm{g\,dm^{-3}}$; initial pH = 5.2.

equilibrium was attained. For Ni^{2+}, this effect of an initial decrease of the pH was less expressed but obviously existed. In the rest of the process, nickel behaved regularly, *i.e.*, the pH increased with time. The subsequent increase in pH could only mean the simultaneous bonding of released protons, as well as the ones already present in

Table 1
Rate constants k_a and the metal uptake q_e for the adsorption of metals onto sawdust.

Parameter	Metal					
	Cd	Cu	Fe	Mn	Ni	Zn
k_a $(\mathrm{g\,mg^{-1}\,min^{-1}})$	0.343	3.69	9.5	6.82	0.2	2.16
q_e $(\mathrm{mg\,g^{-1}})$	2.45	1.9	0.35	1	1.1	1.425
R^2	0.997	0.999	1	1	0.995	1

the aqueous phase. During the adsorption of the other studied metals Zn, Mn, and Fe (Fig. 2b), no decrease in pH was observed as in case of the ones presented in Fig. 2a. On the contrary, the pH value commences increasing right from the beginning of the process, reaching equilibrium and denoting that the adsorption of H^+ ions, known as a very strong competing adsorbate, is a process parallel to the adsorption of metal ions. It turns out that the proposed process stoichiometry, described by Eq. (6), relates only to some particular ions and during the period of time when the concentration of metal ions in the aqueous phase is higher than the concentration of protons. Increasing acidity of the aqueous phase leads to a significant decrease in the adsorption capacity of metal, which will be showed and discussed in the later text. Coincidentally, the authors proposing this mechanism mainly operated with copper ions and did not mon-
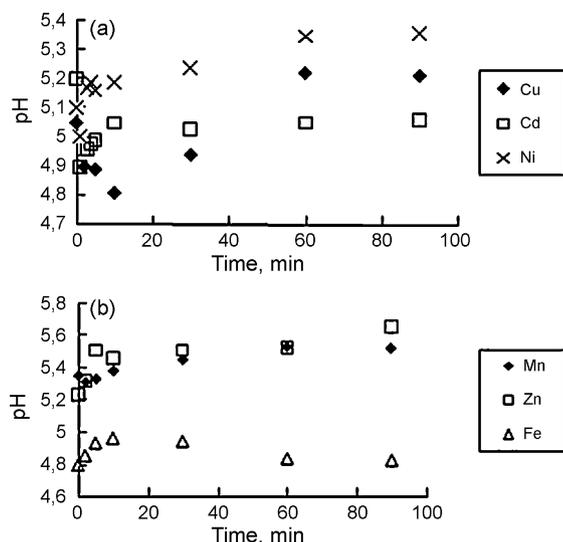
Fig. 2. (a and b) Change of the pH *vs.* time: linden sawdust; $C_{sd} = 20\,g\,dm^{-3}$; particle size < 0.4 mm; initial metal concentration $C_i = 0.05\,g\,dm^{-3}$.

itor the pH change with time [25–27,29,35]. An interesting approach in explaining the mechanism of metal chemisorption onto wooden adsorbents has been described by Fiol *et al.* [20] and Villaesusa *et al.* [40], which allows the possibility of an ion exchange mechanism of metal bonding that occurs by substituting alkali and alkali-earth metals contained in the molecular structure of the adsorbent with heavy metals from the aqueous phase.

Such a change of the pH with time could be explained by adopting the ion exchange mechanism developed by Villaesusa *et al.* [40]. To ascertain the role of alkali and alkali-earth metals in the ion exchange mechanism of sorption, each kind of sawdust (1 g) was stirred with 0.1 M of sulphuric acid (50 ml) for 60 min, then filtered and the filtrates were analyzed for Na^+, K^+, Ca^{2+} and Mg^{2+}. The obtained results are presented in Table 2. As a blank experiment, distilled water mixed with sawdust was used and these results are also presented in Table 2 in brackets. The obtained results clearly show the presence of the considered ions in the filtrates. Of them, a considerable amount of potassium (approximately 75%) is self-leaching with pure water rather than with sulphuric acid solution. Apparently, there is a strong interaction between sawdust and sulphuric acid solution, confirming the replacement of alkali-earth rather than alkali metals from sawdust by protons accordingly to the stoichiometric equation:

$$-RM + zH^+ \Leftrightarrow -RH_z + M^{z+} \tag{7}$$

In the presence of heavy metals in the aqueous phase, it is possible to assume the following stoichiometric equation of the ion exchange process between the solid and liquid phase, supporting the theory of Villaesusa *et al.* [40]:

$$\frac{2}{z}(-RM) + Me^{2+} \Leftrightarrow (-R)_{2/z}Me + \frac{2}{z}M^{z+} \tag{7a}$$
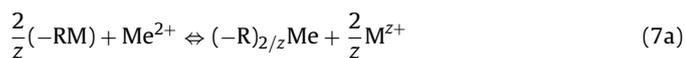
where M is alkali or alkali-earth metal existing in the wood molecular structure; Me denotes heavy metal to be adsorbed; z is number

Table 2
Concentration of alkali/alkali-earth metals in filtrates after sawdust treatment with 0.1 M sulphuric acid solution (open figures) and with water (in brackets).

Kind of sawdust	Na^+ ($mg\,dm^{-3}$)	K^+ ($mg\,dm^{-3}$)	Ca^{2+} ($mg\,dm^{-3}$)	Mg^{2+} ($mg\,dm^{-3}$)
Linden	0.6 (0.13)	24 (18)	30 (7.1)	4.8 (1.2)
Poplar	1.5 (1.5)	25 (18)	45 (5.8)	4.8 (0.6)
Beech	0.5 (0.35)	23 (17)	30 (1.7)	6 (0.6)

of positive charge. Thus, the role of alkali-earth metals contained in plant wastes on the heavy metal adsorption is evident but not yet fully explained.

Nevertheless, data of the pH change during the adsorption process, such as those presented in Fig. 2, have not hitherto been published in the relevant literature and such behaviour deserves to be considered much more for a better understanding the ion exchange mechanism of metal adsorption on sawdust. From an engineering point of view, the change of pH with time is small and could be neglected in consideration and development of the process on a larger scale.

3.3. Effect of the initial pH of solution on the adsorption uptake of sawdust

The initial pH of metal solutions has been recognised by many authors as the major parameter controlling metal adsorption processes [3,12,20,24,26,27,32,36,40]. This is mainly due to the fact that protons are strong competing adsorbate ions and partly due to the fact that the pH of a solution influences the ionization of the functional groups of the adsorbents and the chemical speciation of the metal ions in solution.

In order to study the influence of pH on the adsorption of copper on different kinds of sawdust, a series of adsorption experiments were performed using the adsorption of copper ions as the model-system by varying the initial pH of solution from 0.8 to 5.3. The adjustment was made by adding sulphuric acid to the stock solution. The initial concentration of copper ions was kept constant ($C_i = 0.2\,g\,dm^{-3}$) as well as the other process variables: stirring speed, concentration of sawdust, particles size and time of adsorption, that was 60 min, *i.e.*, long enough to consider the system had attained equilibrium (see Fig. 1). The results are shown in Fig. 3.

It can be observed that the initial pH value greatly influenced the adsorption capacity of used adsorbents, which exhibited a similar trend, *i.e.*, it increased with increasing initial pH, from its zero value at the lowest, here used, pH to its maximum at a certain pH in the range between 3.5 and 5 for all the employed adsorbents. The constant or a even a slight decrease in the adsorption at pH values > 5.5 is due to the formation of soluble copper hydroxyl complexes and copper hydroxide precipitate [24,30]. It can also be noticed from Fig. 3 that all three kinds of sawdust have almost the same capacity to adsorb copper ions. From the results, it is confirmed that the metal adsorption mechanism is ion exchange. The decrease of the adsorption capacity at lower pH values is apparently due to the higher concentration of H^+ ions present in the reaction mixture, which compete with the Me^{2+} ions for the adsorption sites of sawdust. At pH ≤ 1, when the adsorption capacity has zero value, the existence of relatively high proton concentration may cause the occupation of active sites squeezing out the already adsorbed metal ions, thus changing the direction of the ion exchange equilibrium
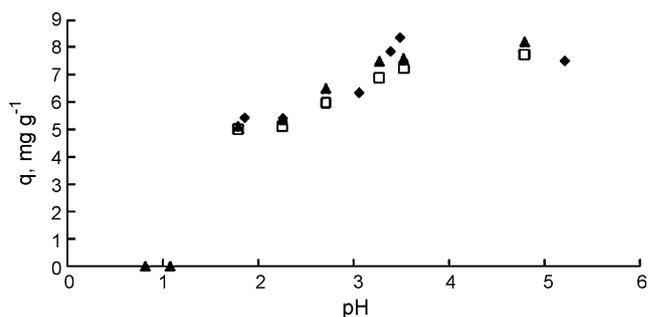

Fig. 3. Change of the adsorption capacity of sawdust against the initial pH value of aqueous phase; sawdust: ▲, poplar; ♦, linden; □, beech; $C_{sd} = 20\,g\,dm^{-3}$; particle size < 0.4 mm; initial metal concentration $C_i = 0.2\,g\,dm^{-3}$.

back towards the starting material. At higher pH values, the concentration of H$^+$ is smaller, and the active sites on the sawdust surface mainly turn into their dissociated forms and can exchange alkali or alkali-earth ions from the adsorbent with the heavy metal ions from solution. This is in accordance with the earlier observations of Shiewer and Volesky [14].

From an engineering point of view, it is important to note that the stripping of adsorbed metal from the loaded sawdust can be performed by more acidic solutions, transferring the adsorbed heavy metals from the adsorbent back into the aqueous phase.

3.4. Adsorption isotherms

The equilibrium between an adsorbate immobilized on the active sites of an adsorbent and the absorbate remaining in aqueous phase is usually presented by adsorption isotherms. In order to describe the adsorption characteristics of low-cost sorbents used in water and wastewater treatment, experimental equilibrium data are most frequently modelled by the relationships developed by Freundlich and Langmuir. Heavy metal adsorption from synthetic solutions was also here tested using these two relationships. The Langmuir isotherm is given by the following equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (8)$$

the linearization of which leads to the following form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \qquad (9)$$

The Freundlich adsorption isotherm, which is an empirical equation, is given as follows:

$$q_e = K_f C_e^{1/n} \qquad (10)$$

the linear form of which can be written as:

$$\log\ q_e = \log K_F + \frac{1}{n} \log C_e \qquad (10a)$$

where C_e is the equilibrium concentration of metal ions (mg dm^{-3}), q_m is the amount of metal ions required to form a monolayer onto the adsorbent surface (mg g^{-1}), K_L is the Langmuir equilibrium constant which is related to the heat of adsorption by equation:

$$K_L = K_o\ \exp\left(\frac{Q}{RT}\right), \qquad (11)$$

where Q is the heat of adsorption, R is the universal gas constant and T is the temperature; K_F and n are the Freundlich equilibrium constant and exponent, respectively.

3.4.1. Adsorption isotherm curves—experimental facts

The distribution of metal ions between an adsorbent and the aqueous phase at equilibrium is of importance to determine the maximum adsorption capacity of the adsorbent for a particular metal ion. In order to obtain evidence concerning the adsorption of heavy metals on sawdust, a series of the equilibrium experiments were performed by mixing equal quantities of linden sawdust (1 g) with equal volumes of solutions (50 ml) containing different concentrations of metal ions in the range from 5 to 200 mg dm^{-3} (initial pH = 5.1). The mixtures were stirred at 300 rpm for 60 min; then filtered and the filtrates analysed for the remaining part of the metal, as described in the experimental part. The adsorption isotherm results, for all considered ions, are shown in Fig. 4 (left column). Linear Langmuir plots were drawn using Eq. (9) and presented in Fig. 4 in the right column next to the corresponding isotherm. From the slopes, q_m was evaluated for each metal, while from the intercepts the equilibrium constant K_L values were computed. A similar linearization procedure was performed out using Eq. (10a) for the

Freundlich model and the associated parameters K_F and n were calculated. The adsorption isotherm parameters are summarized and presented in Table 3, together with the regression coefficients R^2, for both considered models. Since the adsorption degree of Fe^{2+} ions was low, less than 10%, as shown in the text given below, the adsorption isotherm for this ion was not determined and considered here.

According to the regression coefficients, the experimental results for adsorption isotherm provide a better fitting to the Langmuir model for all the considered metal ions. A similar conclusion was reached by other scientists dealing with metal adsorption on sawdust [19,20,36,40], while some others when modelling the adsorption, found a good fit with both the Langmuir and Freundlich equation [25,27,29,34].

3.5. Effect of other process parameters affecting the adsorption

The effectiveness of the adsorption process depends, beside the process time and the initial pH, on many other parameters, such as the initial concentration of metal ions, the kind of metal ions, the size of the particles and concentration of sawdust. Influence of each of these parameters will be presented and discussed in the coming text with the aim of ascertaining how and how much each of them affects the process as well as to provide data necessary for an engineering design of metal ion adsorption on sawdust.

3.5.1. Effect of ion species on the adsorption—selectivity of the process

From an engineering point of view, it is important to obtain evidence concerning the ability of sawdust to adsorb different heavy metals expressed *via* the adsorption degree (AD%) defined by Eq. (2) and to acquire more data about the selectivity of the adsorbent for some particular ions. The adsorption degree of different metal ions *vs*. time is presented in Fig. 5.

Obviously, the adsorption degree follows the shape of the kinetic curves and increases sharply with time reaching, after 10–20 min, a steady state after which the adsorption degree no longer changes with time. The adsorption degrees at the plateau values differ for different ions, giving evidence about the adsorption ability and the percentage which can be achieved by the considered sawdust for each of the considered ion species. According to Fig. 5, the highest adsorption ability was for copper, where an AD of almost 80% was achieved, while the adsorption of iron does not exceed 10%. Ranking the adsorption ability for the other considered ions, the following series is obtained: Cu^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+} > Mn^{2+} > Fe^{2+}.

3.6. Effect of particle size

In order to see how particle size affects the adsorption, a series of experiments was performed using linden sawdust and copper adsorption as the model-system. The averaged particles size was changed from 0.2 to 1 mm keeping the other variables constant as they were in the adsorption isotherms experiments. The obtained results of the adsorption degree, defined by Eq. (2), against the average particle size are plotted in Fig. 6.

Obviously, there is no remarkable effect of the used particles size on the attained adsorption degree, which can be considered as being independent of particles size. The sawdust particles had a flaky shape, as is illustrated by the photograph in Fig. 7. Such irregular shape of particles, having a small shape factor ($\psi \approx 0.126$) [42], means that their geometrical surface is 8–10 times higher than spherical particles of the same volume. Here the shape factor ψ, known also as sphericity in the relevant literature, is defined as the ratio of surface area of sphere of equal volume as particle and
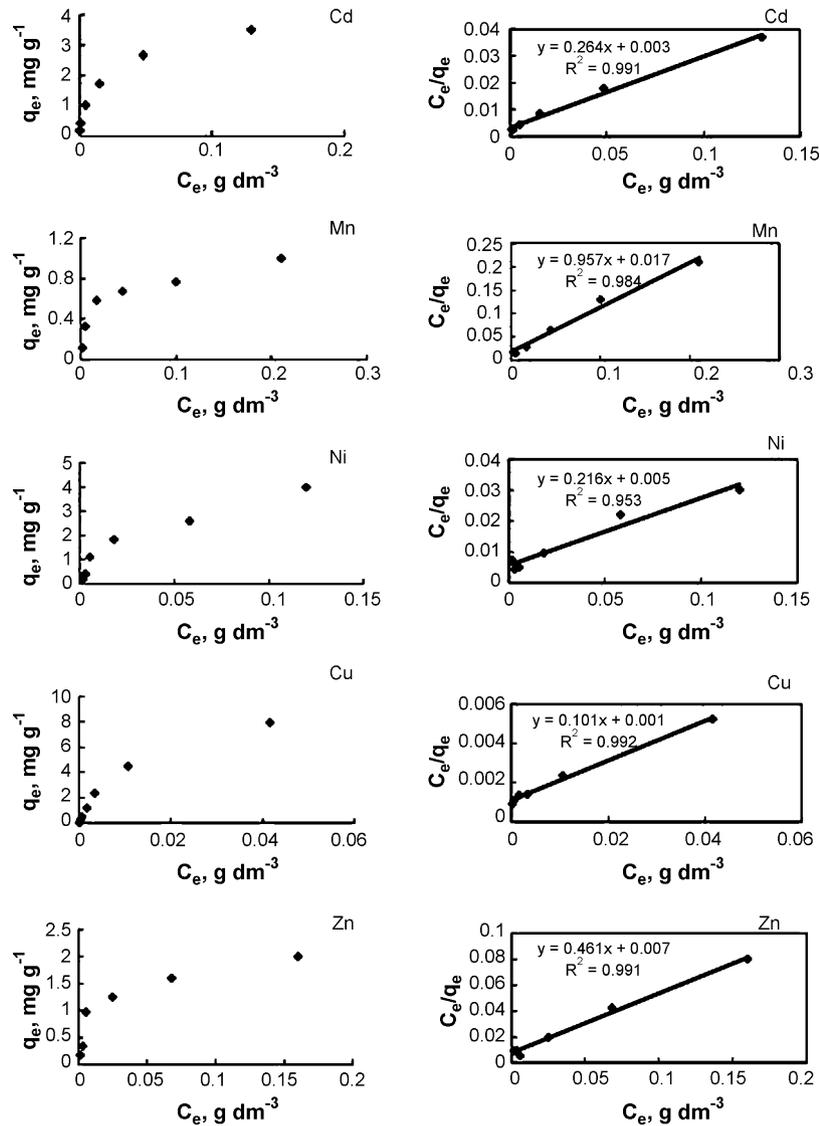
Fig. 4. Adsorption isotherms (left) and their linear Langmuir plots (right) for each considered ion: linden sawdust: particle size < 0.4 mm; $C_i = 0.2$ g dm^{-3}; $C_s = 20$ g dm^{-3}.

surface area of particle:

$$\psi = \frac{A_s}{A_p} \qquad \text{for } V_s = V_p \tag{12}$$

where A_s and A_p are surface area of sphere and particle, respectively. V_s if sphere volume while V_p is volume of particle.

Bearing this in mind, it can be assumed that sawdust particles have developed both an external (due to their flaky shape) and an internal surface (due to their porous structure) which is easily accessible for the penetration of the aqueous phase, bringing heavy metal ions to the active adsorption sites. Changing the particle size in the chosen sieve fractions, particles size range from 0.1 to 1 mm, does not change significantly the real surface area and the

Table 3
Equilibrium parameters evaluated from the adsorption isotherm data.

Metal	Zn	Ni	Cd	Mn	Cu
K_L (dm^3 mg^{-1})	60.72	38.14	14.3	45.9	92
q_m (mg g^{-1})	2.17	4.6	3.5	1.0	9.9
R^2	0.99	0.95	0.997	0.98	0.99
K_F	6.25	21.65	11.5	2.21	1.92
n	2.04	1.5	2.04	2.42	2.26
R^2	0.835	0.926	0.965	0.862	0.98

adsorption degree remains almost constant with changing particles size.

3.6.1. Effect of the initial concentration of metal ions

An important parameter in the adsorption process is the initial concentration of metal ions in the aqueous phase. With increasing the initial concentration of adsorbing ions the plateaux, corre-
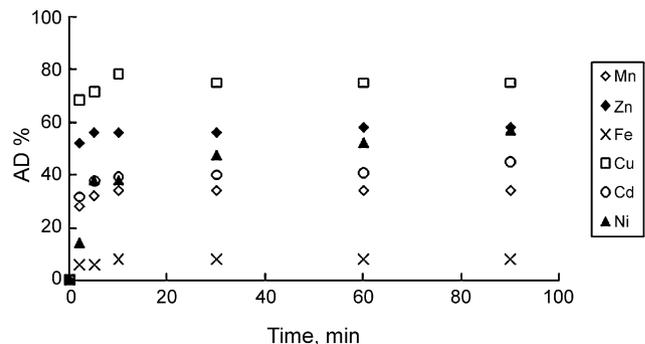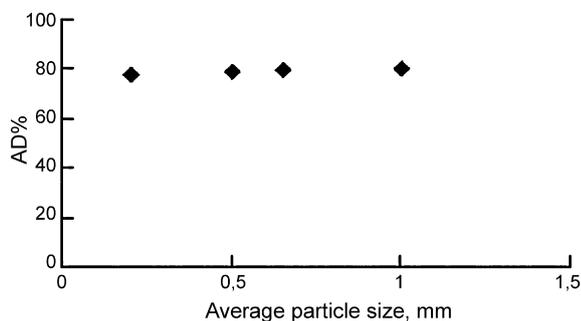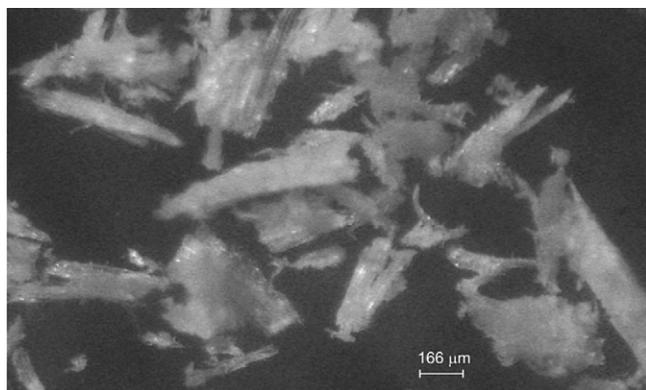

Fig. 5. Adsorption degree (AD%) *vs.* the process time: $C_{sd} = 20$ g dm^{-3}; $C_i = 0.05$ g dm^{-3}; pH 5.2; particle size < 0.4 mm.

Fig. 6. Influence of the particle size on the adsorption of copper ions: linden sawdust $C_{sd} = 20\,g\,dm^{-3}$; pH 5.1; $C_i = 0.2\,g\,dm^{-3}$; particle size < 0.4 mm.


**Fig. 7.** Optical photograph of the linden sawdust: particle size < 0.4 mm.

sponding to the adsorption capacity is shifted towards higher values, as is presented in Fig. 8 for the system copper-sawdust. The shape of curves remained identical but it should be pointed out that the initial concentration influenced the rate of the process rate, *i.e.*, with increasing the initial concentration the rate increased proportionally. This proportionality arises from the definition equation of the adsorption capacity (1) as well as from the process rate given by Eq. (3). For the steady state, when the process rate has zero value, it is easy to verify that the maximum adsorption capacity ratio will be directly proportional to the initial concentration ratio, *i.e.*:

$$\frac{q_{e1}}{q_{e2}} = \frac{C_{i1}}{C_{i2}} \tag{13}$$

Similar results were published by Yu *et al.* [26] and Larous *et al.* [29]. It is clear that Eq. (13) has a limited relevance defined by q_m, *i.e.*, the amount of metal ions required to form a monolayer on the surface of the adsorbent.
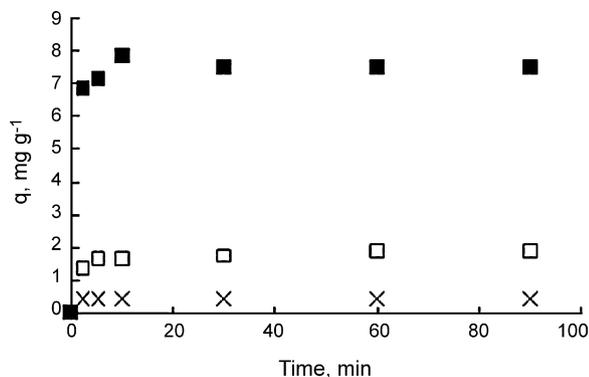
Fig. 8. Effect of the initial concentration of copper ions on the adsorption capacity: linden sawdust $C_{sd} = 20\,g\,dm^{-3}$; pH 5.1; ■, 0.2 g dm^{-3}; □, 0.05 g dm^{-3}; ×, 0.01 g dm^{-3}; particle size < 0.4 mm.
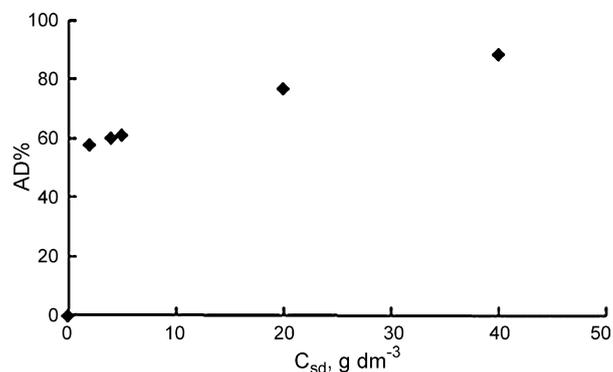
Fig. 9. Effect of sawdust concentration on the adsorption degree of copper ions on linden sawdust: initial pH 5.1; initial concentration of Cu^{2+} is 0.2 g dm^{-3}; particle size < 0.4 mm.

3.6.2. Effect of sawdust concentration—liquid to solid ratio

The sawdust concentration was changed in the range from 2 to 40 g dm^{-3} and the results of this series of experiments are presented in Fig. 9, in which the adsorption degree *vs*. sawdust concentration is plotted. On increasing the sawdust concentration in the suspension, the available surface is increased proportionally; resulting in an increased adsorption degree which was over 90% for the highest concentration of sawdust used in these experiments, thus the concentration of metal in the aqueous phase was lowered after completion of the process. At lower concentrations of sawdust in the suspension, smaller adsorption degrees were achieved due to saturation of the adsorbent when no more ions could be adsorbed. In column tests, in which the sawdust existed in a great surplus, adsorption degree exceeding values of 99.6% with an outlet concentration of copper ions less than 0.01 mg dm^{-3} were achieved with a single pass of the aqueous phase [43].

4. Conclusions

The sawdust of deciduous trees considered in this study appears to be promising adsorbent not only for the efficient removal of copper ions but also, to a lesser extent, for the removal of other heavy metals as: Zn^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+}, Fe^{2+} from weakly acid sources, such as mine waters, rinse waters from electroplating and metal working industry, and similar effluents.

The adsorption of metals is strongly dependant on the process time, pH of the aqueous phase, kind of ions to be adsorbed, the initial concentration of metals and the amount of sawdust. The particles size of the sawdust does not affect the process.

The adsorption kinetics is fast and after 10–20 min of contact time, the system is close to equilibrium. The kinetics can be fairly considered as pseudo-second order reaction. The initial pH value of the solution increases with time, indicating the simultaneous adsorption of metal ions and protons during the process competing for the active sites in the sawdust structure. The ion exchange mechanism was confirmed assuming that alkali-earth metals from the adsorbent were substituted by heavy metal ions and protons. The maximum metal uptake (7–8 mg g^{-1} of sawdust) for each kind of sawdust was obtained at pH values between 3.5 and 5.5. All three kinds of sawdust have almost the same capacity to adsorb heavy metal ions. Acidification of the aqueous phase leads to a decrease in adsorption capacity of sawdust due to an increased proton concentration occupying the active sites in the adsorbent structure. The adsorption of metals is terminated at a pH close to unity.

For a single metal ion system, the adsorption equilibrium data can be modelled by Langmuir adsorption isotherm for all the considered ions and sawdust combinations.

The highest adsorption degree at equilibrium was obtained for copper, for which a value close to 80% was achieved, while the adsorption of iron did not exceed 10%. Ranking the ability of sawdust to adsorb the other considered ions, the following series was obtained: $Cu^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+} > Mn^{2+} > Fe^{2+}$. The adsorption capacity increased with increasing the initial concentration of adsorbate in the aqueous phase.

Increasing the concentration of sawdust in the suspension increased the adsorption degree due to an increased number of active sites available to adsorb metal ions.

Through this study, essential kinetics and thermodynamic data were collected for an engineering design of the column adsorption of heavy metals by sawdust from real solutions.

Acknowledgements

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