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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 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 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 (≈l 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 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 peals, 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.