Application of waste materials as potential biosorbents for Cu(II) and Zn(II) removal

M. Holub
Laboratory of Excellent Research, Faculty of Civil Engineering, Technical University of Kosice
Park Komenskeho 10A, 042 00 Kosice, Slovakia
E-mail: marian.holub@tuke.sk

M. Balintova, S. Demcak, P. Pavlikova
Institute of Environmental Engineering, Faculty of Civil Engineering, Technical University of Kosice
Vysokoskolska 4, 042 00 Kosice, Slovakia

CrossRef http://dx.doi.org/10.5755/j01.ct.67.1.15003

Received 17 May 2016; Accepted 13 July 2016

Mining is probably the most common activity that fundamentally impacts the country. The problems connected with the extraction of sulphide ores arise especially during the final stage of mining, closure and abandonment of the extraction area, when the conditions for the generation of strong acid water are most likely to occur.

With respect to the diversity of compounds in acid mine drainage (AMD) and its low pH values it is hard to find an effective and inexpensive “active” treatment process. Recently, numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of heavy metals and to improve the quality of the treated effluent. Adsorption has become one of the alternative treatments; in the recent years, the search for low-cost adsorbents that have metal-binding capacities has intensified.

Adsorption of heavy metals (Cu and Zn) from single-component aqueous solutions onto non-modified poplar sawdust, hemp shives and peat has been studied using the batch-adsorption techniques. For this purpose, solutions with different concentrations ranging from 10 to 150 mg/L have been used. The study was carried out to examine the adsorption capacity of the low-cost waste materials as potential biosorbents for the removal of heavy metals from acid mine drainage. The adsorption isotherms could be better fitted by the Langmuir model (values of the correlation factor range from 0.974 to 0.997). The values of the separation factor (R_L) in the present study were found to be within 0.037–0.728, indicating the favorable adsorption process. From the comparison of maximum sorption capacities, it is evident that the best adsorption properties are exhibited by the hemp shives, and copper is overall better adsorbed than zinc (Q_max = 12.84 mg/g and 8.28 mg/g for copper and zinc, respectively). The results indicate that these freely abundant, low-cost waste materials can be treated as economically viable for the removal of metal ions in acidic conditions.

Key words: peat, hemp, sawdust, biosorption, acidic conditions

Introduction

Acidic sulfur-rich wastewaters are the by-products of different industrial operations such as galvanic processing and the scrubbing of flue gases at power plants [1]. The major producer of such effluents is, however, the mining industry [2]. Resulting from the fact that they often contain elevated concentrations of metals (iron, aluminium, zinc or copper) and metalloids (most often arsenic), such waters typically pose an additional risk to the environment and can cause ecological destruction in river basins and the contamination of water resources.

The commonly used procedures for removing metal ions from effluents result from the need by industry to achieve acceptable effluent quality standards set by the local governments. It includes chemical precipitation, ion exchange, lime coagulation, reverse osmosis, membrane separation, solvent extraction, etc. [3]. Most of the above-listed techniques, being economically expensive, have several disadvantages such as incomplete metal removal at low concentrations, high energy requirements, complicated regeneration, and the generation of toxic sludge or other waste by-products that require further disposal or deposition [4].

For this reason, cost-effective alternative and environmental-friendly technologies or sorbents for the treatment of metals-contaminated waters are needed to be developed.

Due to their availability and low cost, the search has led to the investigation of materials of agricultural and biological origin, along with industrial by-products, as the potential metal sorbents that can be widely used without expensive regeneration [5, 6]. Natural materials are available in large quantities, or certain waste products from industrial or agricultural operations include rice bran, soybean and cottonseed hulls, sunflower stalks, wheat shell, cactus leaves, grape stalk waste, pine needles, almond shell, olive cake, canola meal, pine bark, moss, etc.

The main constituents of lignocellulosic materials are cellulose, hemicelluloses, lignin carbohydrates, and phenolic compounds which have carboxyl, hydroxyl, sulfate, phosphate, and amino groups responsible for metal ion binding.
The term “biosorbent” is an alternative to the conventional methods and represents the usage of dead biomass as well as living plants or even bacteria as sorbents.

The present study is focused on the utilization of waste-adsorptive materials based on dead biomass for removing heavy metal ions from model acidic solutions. The adsorption of copper and zinc from single-component aqueous solutions onto non-modified poplar sawdust, hemp shives and peat has been studied using batch-adsorption techniques.

**Materials and methods**

As a sorptive material, in experiments the commercial peat “PEATSORB” (REO AMOS Slovakia), hemp shives (provided by Hempflax, the Netherlands) and poplar wood sawdust (provided by a local producer of wood products) were used. The sorbents were used in their natural state, without any chemical or physical modification. All sorbents were dried at 105 °C for 2 h and then allowed to cool in desiccators before use.

To determine changes in the concentrations and pH, following apparatus were used:

- a colorimeter DR890 (HACH LANGE, Germany) with appropriate reagents was used to determine the concentration of dissolved copper (the Bicinchoninate method; deviation ±0.02 mg/L) and zinc (the Zincon method; deviation ±0.02 mg/L);  
- pH was determined by a pH-meter FiveGO-FG2 (METTLER TOLEDO, Switzerland) which was standardized using buffer solutions of different pH values (4.01, 7.00).

Single-component model solutions were prepared by diluting to the desired initial concentration (10, 30, 50, 70, 90, 110, 130 and 150 mg/L) a concentrated stock solution of copper and zinc, prepared by dissolving copper (II) sulfate pentahydrate and zinc (II) sulfate heptahydrate in deionized water. The initial pH of each solution was adjusted to the required value (pH = 4.0–4.1) by adding 0.001 M H₂SO₄.

Sorption studies were conducted by the batch technique at room temperature (23 ± 0.2 °C) in beakers by adding a constant mass of a sorbent (1.0 g) to 100 mL of the solution.

In order to obtain data for isotherms study, various solutions with the initial Cu(II) or Zn(II) concentrations ranging from 10 to 150 mg/L (10, 30, 50, 70, 90, 110, 130 and 150) were prepared. Adsorbates were contacted with an adsorbent for 24 hours of the reaction time. At the end of the contact time, the solid was removed by filtration through a laboratory filter paper for the qualitative analysis, and the equilibrium concentrations were determined. In all experiments, the pH was measured at the beginning and at the end of sorption.

To calculate the adsorption capacities, the following equation was used:

\[ q_e = \frac{(c_0 - c_e) \times V}{m} \]  

where \( q_e \) – adsorption capacity per unit mass of adsorbent, mg/g; \( c_0 \) – the initial concentration of the appropriate metal ions, mg/L; \( c_e \) – the equilibrium concentration of the appropriate metal ions, mg/L; \( V \) – the volume of the aqueous phase, L; \( m \) – the mass of the adsorbent, g.

For the purpose of isotherm data analysis, the Freundlich and Langmuir equilibrium theories are discussed in this paper. The equilibrium sorption data were analyzed using the DataFit 9.0.59 and OriginLab 2016 programs.

Differences in FTIR measurements of all biosorptive materials were determined with an Alpha Platinum-ATR spectrometer (BRUKER OPTICS, Ettlingen, Germany). A total of 24 scans were performed on each sample in the range of 4000–400 cm⁻¹.

A specific surface area as a significant sorption parameter was estimated by low-temperature gas adsorption using nitrogen gas (Quantachrome NOVA 1000e, USA).

**Infrared spectra of materials**

The Fourier transform infrared spectroscopy (FT-IR) is most useful for providing information about molecular fragments, the presence or absence of specific functional groups. This method has several advantages against other research methods such as UV/Vis spectroscopy or CHNS analysis. The general advantage is the simplicity of this method. The application of FT-IR spectroscopy provides data about the nature of oxygen- and hydrogen-containing functional groups, their structural array, relations, etc. [7, 8]. The FT-IR spectra of the samples show an almost similar structure (Fig. 1.), which is caused by their composition formed by hemicellulose, cellulose, and lignin. In the case of peat, some differences can be observed in the area 1200–1500 cm⁻¹, which is caused by cellulose content. The proportion of cellulose present in peat will typically decrease with increased levels of humification.

According to the fundamentals of infrared spectroscopy, the middle range of the IR spectrum, which is comparable with peat, can be generally separated into three zones [9]:

1. The R-H region (4000–2500 cm⁻¹). It is typical for O–H, NH and C–H absorption bands.
2. Absorption within the range from 2000 to 1500 cm⁻¹ is characteristic for functional groups with double bonds. Usually these are C=O and C≡C.
3. An absorption area below 1500 cm⁻¹ is called the “fingerprint region”. In this region, there fluctuate functional groups with a wide non-specific absorption range. Typically, in this area polysaccharide absorption bands can be observed, mostly around 1040 cm⁻¹.

The major bands observed in the FT-IR spectra of hemp shives and their assignments to the vibrations of chemical groups and molecules are summarized in Table 1. [10].

The structure of wood sawdust exhibits a strong broad OH stretching at wavenumbers 3700–3200 cm⁻¹, which can be caused by the presence of water or moisture, too. The C–H stretching of methyl and methylene groups is observed at 3000–2800 cm⁻¹. For the C=O bond from the acetyl groups, typical is the stretching band at 1731 cm⁻¹ [11]. The characteristic bands of lignin were confirmed at
1503 and 1452 cm\(^{-1}\) wavenumbers (aromatic skeletal vibrations of lignin) and at 1320 cm\(^{-1}\) (syringyl and guaiacyl condensed lignin) [12]. Wavenumbers at 1422, 1367, 1315, 1024 and 894 cm\(^{-1}\) appertain to cellulose in the crystalline and amorphous form. The functional groups of aromatics, carboxylic acids, alkyl halides were found at 828 cm\(^{-1}\). At 554 cm\(^{-1}\), also alkyl halides were determined [11, 12].

The infrared spectrum of peat shows an intensive deformation in the area 3700–3300 cm\(^{-1}\) representing a strong broad OH\(^{-}\) stretching. The functional groups of aliphatic C–H, CH\(_2\), CH\(_3\) stretching were found at 2950–2850 cm\(^{-1}\). At 1640–1725 cm\(^{-1}\), the C=O stretching of carboxylic acids was determined. The aliphatic C–H deformation, OH\(^{-}\) deformations and the C–O stretching of phenolic OH\(^{-}\), the C–H deformation of CH\(_3\) groups and salts of carboxylic acids are present in the area 1470–1330 cm\(^{-1}\). The C–O stretching of esters, ethers and phenols was noted at 1280–1140 cm\(^{-1}\).

![Infrared spectra of biosorbents](image)

**Fig. 1.** Infrared spectra of biosorbents: a – poplar sawdust, b – hemp shives, c – peat

**Table 1.** Functional groups observed in the FT-IR spectra of hemp shive samples

<table>
<thead>
<tr>
<th>Band position, cm(^{-1})</th>
<th>Functional group</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>3340</td>
<td>OH stretching</td>
<td>Polysaccharides</td>
</tr>
<tr>
<td>2897</td>
<td>C–H symmetrical stretching</td>
<td>Polysaccharides</td>
</tr>
<tr>
<td>1733</td>
<td>C=O unconjugated stretching</td>
<td>Hemicellulose</td>
</tr>
<tr>
<td>1636</td>
<td>OH (water)</td>
<td>Cellulose</td>
</tr>
<tr>
<td>1507</td>
<td>C=C symmetrical stretching of the aromatic ring</td>
<td>Lignin</td>
</tr>
<tr>
<td>1454</td>
<td>CH(_2) bending</td>
<td>Lignin</td>
</tr>
<tr>
<td>1422</td>
<td>CH(_3) bending</td>
<td>Cellulose</td>
</tr>
<tr>
<td>1373</td>
<td>CH bending</td>
<td>Cellulose (a)</td>
</tr>
<tr>
<td>1337</td>
<td>OH in plane bending</td>
<td>Cellulose (c)</td>
</tr>
<tr>
<td>1320</td>
<td>CH(_2) wagging</td>
<td>Lignin</td>
</tr>
<tr>
<td>1265</td>
<td>CO stretching</td>
<td>Hemicellulose, pectin</td>
</tr>
<tr>
<td>1157</td>
<td>COC asymmetric bridge oxygen stretching</td>
<td>Polysaccharides</td>
</tr>
<tr>
<td>1028</td>
<td>C–C, C–OH, C–H ring and side group vibrations</td>
<td>Hemicellulose, pectin</td>
</tr>
<tr>
<td>896</td>
<td>Glycosidic bonds symmetric ring-stretching mode</td>
<td>Polysaccharides</td>
</tr>
</tbody>
</table>

**Specific surface area**

One of the many properties used to characterize adsorbents is the specific surface area (SSA). The SSA plays an important role in the adsorption process; however, there are other mechanisms influencing the progress of adsorption (e.g., complexation, ion-exchange abilities, chelation, etc.).

In order to evaluate the differences among the samples, the SSA estimation of by the physisorption of nitrogen gas at 77 K according to the BET method was carried out. Degassing of the samples was carried out with respect to their thermal stability determined by a thermal analyzer (Netzsch STA 449 F3, Germany). The results are presented in Table 2.

As one can see, differences among the samples are minimal, and the SSA is not corresponding with the results of the sorption experiments discussed below. These facts show indicate a different background of the adsorption process.
Table 2. Specific surface areas

<table>
<thead>
<tr>
<th></th>
<th>Sawdust</th>
<th>Hemp shives</th>
<th>Peat</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{BET}$, m$^2$/g</td>
<td>1.52</td>
<td>1.42</td>
<td>1.32</td>
</tr>
<tr>
<td>$C_{BET}$</td>
<td>13.559</td>
<td>80.167</td>
<td>67.132</td>
</tr>
<tr>
<td>R$^2$</td>
<td>0.993</td>
<td>0.998</td>
<td>0.995</td>
</tr>
</tbody>
</table>

Adsortion isotherm

Adsorption is usually described through isotherms, i.e. functions which connect the amount of the adsorbate on the adsorbent. The distribution of metal ions between the liquid and the solid phases can be described by several isotherm models. Most discussed are the Freundlich and Langmuir isotherm models.

The Freundlich equation [13] has been widely used for isothermal adsorption. This is a special case for a heterogeneous surface, and the isotherm is introduced as an empirical model:

$$q_e = k c_e^n.$$  \hspace{1cm} (2)

The equation can be linearized, and the temperature-dependent constants $k$ and $1/n$ are found by linear regressions:

$$ln q_e = ln k + \frac{1}{n} ln c_e;$$  \hspace{1cm} (3)

where $k$ represents the sorption capacity when the metal equilibrium concentration equals to 1; $c_e$ – the equilibrium concentration of metal remaining in the solution, mg/L; $q_e$ – the amount of metal adsorbed per unit weight, mg/g; $n$ – Freundlich constants related to adsorption intensity.

The $n$ value is the indicator of the nonlinearity degree between the solution concentration and adsorption. From equilibrium experiments the $n$ value was found to vary from 1.94 to 4.43 (Tables 3–5) which is the most common situation, and the values of $n$ within the range of 1–10 represent good adsorption [14, 15].

The Langmuir isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical adsorption sites. This model is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of the adsorbate in the plane of the surface [16]. The isotherm is represented by [17]

$$q_e = \frac{Q_{max} b c_e}{1 + b c_e},$$  \hspace{1cm} (4)

or

$$\frac{c_e}{q_e} = \frac{1}{b Q_{max}} + \frac{c_e}{Q_{max}},$$  \hspace{1cm} (5)

where $q_e$ – the amount of metal adsorbed per mass unit of the sorbent at equilibrium, mg/g; $Q_{max}$ – the amount of the adsorbate at a complete monolayer, mg/g; $b$ – the Langmuir constant, L/mg, which relates to the heat of adsorption.

Results and discussion

From the linear plots of specific adsorption ($c_e/q_e$) against the equilibrium concentration ($c_e$) (Fig. 2 and Fig. 3) it is clearly visible that the adsorption follows the Langmuir equation.

For comparison, in Fig. 4 and Fig. 5 the linear plots of Freundlich isotherms are shown. The fit was obtained with a smaller correlation.

The Freundlich and Langmuir adsorption constants and the correlation coefficients ($R^2$) are listed in Tables 3–5. The results show that the Langmuir model is better suitable for the description of the adsorption ($R^2$ values in the range from 0.974 to 0.997).
From the data listed in Tables 3–5 it is clearly visible that the best sorption properties are obtained using the hemp shives. The second most effective sorbent was the peat. In the case of zinc cations, hemp shives are most effective, and the differences between peat and poplar sawdust are very small.

Essential features of the Langmuir adsorption isotherm parameter can be used to predict the affinity between the adsorbate and the adsorbent, using a dimensionless constant called the separation factor. This factor is expressed by the following relationship [18, 19]:

$$R_L = \frac{1}{1 + b \cdot c_i},$$

where $c_i$ – the initial concentration; $b$ – the Langmuir constant. The values between 0 and 1 indicate a favorable adsorption.

The $R_L$ values in the present investigation were found to be 0.037–0.728, indicating that the adsorption of a metal ion onto the used biosorbents was favorable.

### Conclusions

Using waste materials as a replacement of the current costly industrial sorbents is growing in popularity over the last years. Waste materials from industry or agriculture with the satisfactory capacity of heavy metals removal can be obtained, employed, reused or disposed of with a little cost.

The used biosorbents have been shown to be a suitable material for the removal of metals from acidic solutions. According to the Langmuir $Q_{max}$ constant, the best adsorption properties were obtained by hemp shives in both types of a solution containing copper ($Q_{max} = 12.84$ mg/g) or zinc ($Q_{max} = 8.28$ mg/g). From the
results it is also evident that the copper cations are better adsorbed than zinc.

The adsorption isotherms data could be well fitted by the Langmuir model (R² values in the range from 0.974 to 0.997). The values of the separation factor (Rₛ) in the present investigation range from 0.373 to 0.728, i.e. are less than 1, indicating that the adsorption of the metal ion is favorable.

Acknowledgements

This work has been supported by the Slovak Grant Agency for Science (Grant No. 1/0563/15).

References


M. Holub, M. Balintova, S. Demcak, P. Pavlikova

ATLIEKŲ KAIP BIOSORBENTŲ Cu(II) IR Zn(II) ŠALINTI PANAUDOJIMO TYRIMAS

Santrauka

Pavieniai sunkiųjų metalų (Cu ir Zn) adsorbciją vykdyta vandeninėje terpėje, naudojant nemodifikuotas tuopos pjuvenas, kanapių spalų iš nuotekų, panaudojant juos kaip biosorbentus. Nustatyta, kad adsorbcijos izotermes geriau aprašo Langmuir'o modelis (tiesės reikšmingumo koeficiento vertė kito nuo 0,974–0,997), apskaičiuotos atskirinio faktoriaus (Rₛ) vertės 0,037–0,728, kurios pateko į standartinį adsorbcijos procesus. Nustatyta, kad didžiausia absorbicinė geba tiek vario, tiek ir cinko jonams pasižymi kanapių spalių, tačiau adsorbcijos geba vario jonams yra didesnė (Qₘₐₓ = 12,84 mg/g ir 8,28 mg/g atitinkamai). Gauti rezultatai parodė, kad mažai kainuojančios atliekos gali būti naudojamos ekonomiškam metalų jonų šalinimui iš rūgščių vandeninių terpių.