Sorption of metals on biological waste material

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Abstract
Bioadsorption by materials such as orange peel could be a cost effective technique for removing toxic heavy metals from wastewater. The performance of a new biosorbent system, consisting of an orange peel matrix which was magnetically modified by iron oxide nanoparticles, for the removal of heavy metal ions from an aqueous solution was tested. The use of low-cost and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods. Orange peel is a waste material from food industry and it is a big advantage when compared with current expensive adsorbents. Orange peel was collected from the fields of orange trees and converted into the low-cost adsorbent. This paper deals with the removal of heavy metal ions from aqueous solutions by magnetically modified orange peel. The widely used Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models were utilized to describe the biosorption equilibrium process.

Keywords
orange peel, biosorption, wastewater, heavy metals

INTRODUCTION
Orange as the main citrus fruit is one of top-five fruit commodities that dominate the global production of fruit market. According to Food and Agriculture Organization, global orange production reached 68 million tons representing 8.5% of the total fruit production in the world in 2012 (FAOSTAT, 2016). Approximately, 40–60% of oranges are processed for juice production, of which 50–60% ends up as waste including seed, peel, segment membrane and other by-products (Grohmann et al., 1992). Citrus wastes constitute a severe environmental problem. Among these wastes, citrus peel is the major constituent accounting for approximately 44% of the weight fruit mass (Widmer et al., 2010). A large amount of this waste is still dumped every year (Pourbafrani et al., 2010), which causes both economic and environmental problems such as high transportation cost, lack of dumping site, and accumulation of high organic content material (Tripodo et al., 2004). Therefore, more effective and sustainable alternatives for using orange peel wastes such as adsorbent are highly desirable (Wikandari et al., 2015).

The discharge of industrial and sewage effluents into water streams and soils has become a serious environmental problem. Rapid urbanization and industrialization, especially, in developing countries without considering the environmental implications often lead to environmental contamination with heavy metals. Nowadays, the inputs of the heavy metals in the environment are monitored and are mostly faced by stringent regulations. The removal of such contaminants from waste water have been developed. The predominant applied methods are coagulation, flocculation, precipitation, electrochemical processes, ion exchange, extraction etc. Use of a suitable sorbent is another favourable way of removing pollutants from waste water. Price, availability, adsorption capacity and strong affinity to pollutants are limiting factors for sorbent application in waste water treatment hence new materials to be used as sorbents are evaluated constantly (Rozumová et al., 2016).

Biosorption processes, defined as the sorption of metal ions by biomass, are being employed as an alternative technique for the decontamination of industrial effluents and for the recovery of the retained metals. Different types of biomass have been used for the clean-up of industrial effluents, such as algae, bacteria, fungi, yeasts, ground coffee, nut and walnut shells, papaya wood, peanut hull pellets, teak leaf powder, lalang (Imperata cylindrica) leaf powder, Coriandrum sativum, grape stalks wastes generated in the wine production process, hazelnut shells etc. (Rozumová et al., 2016). Magnetic derivatization of adsorbents is a very important modification which was proven to
improve the manipulation and increase their adsorption capacity; magnetically modified
montmorillonite (Mockovciakova et al., 2010), zeolite (Matik et al., 2004) or bentonite (Oliveira et
al., 2003) have been already used for adsorption of heavy metal ions. Biological materials are
mainly diamagnetic, which means they do not interact significantly with an external magnetic field;
however, their magnetic modification significantly improves the whole adsorption and separation
process.
In the present work, magnetically modified orange peel was used. This biosorbent, composed of
dried peel is easily available (waste from production of orange industries) and has a great potential
for wastewater treatment. This work deeply investigates the biosorption and desorption process
of heavy metals (Ni and Pb). Besides the influence of pH, the sorption biomass uptake has also been
quantified by means of sorption models, namely Langmuir, Freundlich, Temkin and Dubinin-
Radushkevich ones.

MATERIALS AND METHODS

Biomass
Orange peel was collected from locally available orange company and after drying it was ground in
a coffe mill. The particles with diameter less than 0.5 mm were prepared. Water-based ionic
magnetic fluid stabilized with perchloric acid (analytical grade) was prepared using a standard
procedure (Massart, 1981). The ferrofluid was composed of magnetic iron oxide nanoparticles with
diameters ranging between 10 and 20 nm (measured by electron microscopy). The relative magnetic
fluid concentration (25.2 mg.ml⁻¹) is given as the iron (II, III) oxide content determined by a
colorimetric method (Kiwada et al., 1986). Three grams of powdered orange peels in a 50 ml
polypropylene centrifuge tube were suspended in 40 ml of methanol and then 6 ml of ferrofluid was
added. The suspension was mixed in a rotary mixer (Dynal, Norway) for one hour. Then the sample
was rinsed by methanol and dried at laboratory temperature (Safarik et al., 2010).

Adsorption studies
Adsorption studies were carried out using the batch technique to obtain the equilibrium data.
Adsorption studies were conducted in plastic flasks using 100 ml of metal solutions with defined
initial ion concentration and 0.2 g of magnetically modified orange peel. Samples were stirred for
168h at laboratory temperature using overturn shaker. Samples were taken at pre-determined time
intervals (5, 24, 48, 72, 168h) for analysis of residual concentration in solution. The adsorbent was
then separated using 0.45 μm pore size membrane filter and after conservation, metals concentration
were determined. Adsorbent material was dried at laboratory temperature and studied by electron
scanning microscopy; desorption experiment was carried out using the same apparatus as in
adsorption study.
The pH of the metal ion solution was adjusted to values within the range of 3–7.
Experiments were performed using stock solutions of 5 g.l⁻¹ of Ni and Pb prepared from chemical
reagents of analytical grade: NiSO₄·7 H₂O and Pb(NO₃)₂. In the case of Pb, nitrate instead of
sulphate was used to avoid metal precipitation. The initial pH was adjusted with diluted
hydrochloric acid and sodium hydroxide at a concentration of 1 g.l⁻¹ in demineralized water.
The Ni, Pb and Fe concentration in aquatic solution was determined by atomic absorption
spectroscopy with flame atomization AAS-FA (UNICAM SOLAAR M6).

Characterization of biomass
Morphological analysis of the peel was performed by scanning electron microscopy (SEM LYRA3
TESCAN) equipped with energy-dispersive X-ray spectrometer (EDX). Qualitative EDX elemental
analysis was mainly used for recording line scans and elemental maps of the adsorbed metals. The
specific surface area was measured with the Quadrasorb EVO/SI and calculated by the
QuadraWin software according to the BET isotherm. Results were obtained by means of pure liquid N\textsubscript{2} adsorption at 77 K. Prior to analysis, all samples were degassed under vacuum at 40 °C for 12 h. Concentration of Ni, Pb and Fe in aqueous leachates were determined by atomic absorption spectrometer AAS-FA (UNICAM SOLAAR M6).

**Data processing and adsorption isotherms**

The removal percentage of Ni and Pb at equilibrium was calculated by the following Eq. 1:

\[
\text{Removal} (\%) = \frac{c_0 - c_e}{c_e} \times 100
\]

where \(c_0\) is the concentration of the applied metal ions and \(c_e\) is the metal ions concentration at equilibrium, respectively. Metal ions adsorbed (mg.g\(^{-1}\)) on orange peel was calculated for each sorbent by the following Eq. 2:

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

where, \(q_e\) is the amount of adsorbed metal ions (mg.g\(^{-1}\)), \(V\) is the applied metal ions solution volume (l) and \(W\) is the adsorbent weight (g).

Freundlich and Langmuir adsorption isotherms were used in this study for modelling the sorption data of metals Ni and Pb on the studied orange peel under the optimum conditions of pH and contact time obtained from the batch technique.

**RESULTS AND DISCUSSION**

**Orange peels characterization**

The morphological appearance of the magnetically modified orange peel is shown in Fig. 1. The images were taken using electron scanning microscope. By mapping, magnetically modified material was proven to have adsorbed particles of iron oxides on the surface of magnetically modified orange peel. Fig. 1 shows the heterogeneity in the shape and size of the different particles. Different pore sizes may be observed. Fig. 2 shows that Fe and metal were bound on the surface of adsorbent.

Specific surface area of original orange peel without modification was 0.45 m\(^2\).g\(^{-1}\) and after magnetic modification was increased on 1.60 m\(^2\).g\(^{-1}\).

**Figure 1.** SEM images of magnetically modified orange peels before adsorption of metals (left) and after adsorption of Pb (right).
Acidity/alkalinity of the solution is an important factor affecting adsorption of metal ions on adsorbent surface and for controlling the adsorption process. The speciation of metal ions in aqueous phase as well as the dissociation of active functional sites on the biosorbent is governed by solution pH. Effect of pH on adsorption was studied at 10 mg.l\(^{-1}\) metal concentration at ambient temperature between pH values 3 and 7. Effect of pH variation on equilibrium uptake is given in Fig. 3. The adsorption of orange peels increased with pH up to 6–7 for Ni and 4-5 for Pb.

**Effect of contact time**

The adsorption of Ni and Pb on magnetically modified orange peels was studied as a function of contact time to determine the equilibrium time (Fig. 4). Initial concentration of metals was selected on 10 mg.l\(^{-1}\). It was found that within the first 5 hours of contact time about 46% of Ni and 66% of Pb was adsorbed, and thereafter the adsorption rate was speeded up. For both the biosorbents the equilibrium adsorption time was recorded to be 48-72 hours and after that, more or less constant removal of metals Ni and Pb was observed. Therefore, equilibrium time was set conservatively at 168 hours for further experiments. The equilibrium states were attained in 48 hours for 10 mg.l\(^{-1}\) initial metal concentrations.
Effect of initial concentration

The adsorption of metals on magnetically modified orange peel was evaluated as a function of initial concentration ranging from 10 to 1000 mg.L$^{-1}$, at pH 6-7 (Ni) and 4-5 (Pb). As illustrated in Fig. 5 and Fig. 6, when initial concentration of metals increased from 10 to 700 mg.L$^{-1}$, the adsorption capacity encountered a rise from 5 to 167 mg.g$^{-1}$ (Pb) and from 4 to 67 mg.g$^{-1}$ (Ni), while removal efficiency decreased from 93 to 38% (Pb) and from 72 to 14% (Ni). Better adsorption efficiency was observed for low concentration of Ni, where efficiency of removal reached 70%, while for Pb the efficiency of removal for low concentration of metal ions was 90%. At the range of Pb concentrations 50-100 mg.L$^{-1}$ the efficiency of removal reached 80%, and for concentration 200 mg.L$^{-1}$ this value still reached 50%.

In any adsorption process, the initial concentration of metal ions in solution plays a key role as a driving force to overcome the resistance for mass transfer between the aqueous and solid phase. Thus it is expected that the amount of adsorbed Pb and Ni will increase with raising the initial concentration. Unlike adsorption capacity, adsorption efficiency decreased with increasing initial metal concentration. This can be explained by the fact that in lower initial concentrations Pb and Ni could simply attach to the abundant adsorption sites on the surface of magnetically modified orange peel. However, at higher initial metal concentrations, the number of adsorption sites remain the same (the dosage of adsorbent did not change), so the access of Pb and Ni to adsorption sites is limited and as a result the adsorption efficiency decreases.
Figure 6. Effect of initial metal concentration on adsorption capacity of Ni and Pb on magnetically modified orange peels.

Modeling of biosorption isotherms

An equilibrium condition is achieved, when solute concentration remains unchanged as a result of zero net amount of solute adsorbed and desorbed. At the constant temperature, these associations between the equilibrium concentration of the adsorbate in the solid and liquid phase are defined by the equilibrium adsorption isotherms (Kyzas et al., 2015). Therefore in present work, study of adsorption isotherm models was conducted in order to investigate the adsorption behaviour and adsorption capacity required for removing a unit mass of metals Ni and Pb under the system conditions by magnetically modified orange peel. In the present work, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich biosorption isotherm equations were used to find the correlation between the amount of biosorbent and the liquid phase concentrations of the adsorbate.

**Langmuir** model assumes that adsorption occurs at specific homogeneous adsorption sites within the adsorbent and intermolecular forces decrease rapidly with the distance from the adsorption surface. At room temperature the concentration of metal in solution will be in equilibrium with metal ions biosorbed onto the magnetically modified orange peel. The saturated monolayer isotherm can be described by the Langmuir equation as followed (Langmuir, 1916):

\[ q_e = \frac{q_{max} K_L c_e}{1 + K_L c_e} \]  

(1)

where \( c_e \) is the equilibrium concentration (mg.l\(^{-1}\)), \( q_e \) the amount of metal ion sorbed (mg.g\(^{-1}\)), \( q_{max} \) is \( q_e \) for a complete monolayer (mg.g\(^{-1}\)), \( K_L \) is a constant related to the affinity of the binding sites (1/mg). The linearized form of the Langmuir equation is:

\[ \frac{c_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{c_e}{q_{max}} \]  

(2)

The values of \( q_{max} \) and \( K_L \) were computed from the slope and intercept of the Langmuir plot of \( 1/ce \) versus \( 1/q_e \). The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter \( R_L \), which is a dimensionless constant referred to as separation factor or equilibrium parameter (Dada et al., 2012).

\[ R_L = \frac{1}{1+(1+K_L c_0)} \]  

(3)

where \( c_0 \) is initial concentration. \( R_L \) value indicates the adsorption nature to be either unfavourable if \( R_L > 1 \), linear if \( R_L = 1 \), favourable if \( 0 < R_L < 1 \) and irreversible if \( R_L = 0 \).

From the data calculated in the Table 1, the \( R_L \) is greater than 0 but less than 1 indicating that Langmuir isotherm is favourable. From this research work, the maximum monolayer coverage capacity (\( q_{max} \)) from Langmuir isotherm model was determined to be 181.8 mg.g\(^{-1}\) (Pb) and 142.8 mg.g\(^{-1}\) (Ni), \( K_L \) (Langmuir isotherm constant) are 0.010 l.mg\(^{-1}\) (Pb) and 0.001 l.mg\(^{-1}\) (Ni), and the \( R^2 \) value are 0.953 (Pb) and 0.200 (Ni) proving that the sorption data of Pb fitted well to Langmuir isotherm model.

The **Freundlich** equation accounts for a multisite adsorption isotherm for heterogeneous surfaces.
and is characterized by the heterogeneity factor \(1/n\). Freundlich \(K_F\) constant indicates the biosorption capacity of the biosorbent and constant \(n\), the state of affinity of biosorption of the biosorbent with the sorbate (Gohari et al., 2013). These data often fit the empirical equation proposed by Freundlich:

\[
q = K_F \cdot c^{1/n}
\]

where \(q\) (expressed in \(\text{mg.g}^{-1}\)) is the amount of metal ion adsorbed per unit mass of adsorbent, \(K_F\) and \(n\) are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively, and \(c\) is the concentration of unadsorbed metal ion in final solution at equilibrium (Rozumová et al., 2016). The constant \(K_F\) is an approximate indicator of adsorption capacity, while \(1/n\) is a function of the strength of adsorption in the adsorption process. If \(n = 1\) then the partition between the two phases are independent of the concentration. If value of \(1/n < 1\) it indicates a normal adsorption. On the other hand, \(1/n > 1\) indicates cooperative adsorption (Voudrias et al., 2002). A plot of \(\log q_e\) versus \(\ln c_e\) gives a straight line with the slope \((1/n)\) and intercept \((\log K_F)\).

The estimated constants \(K_F\) and \(n\) were represented in Table 1 and fitted isotherm was shown in Fig. 7. However, \(K_F\) and \(n\) are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of isotherm models. Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate sorption data where \(1/n\) is a heterogeneity parameter, the smaller \(1/n\), the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when \(1/n = 1\). If \(n\) lies between one and ten, this indicates a favorable sorption process (Goldberg, 2005). From the data in Table 1, that value of \(1/n = 0.516\) while \(n=1.938\) for Pb and value of \(1/n = 1.303\) while \(n=0.767\) for Ni\(^{2+}\) indicating that the sorption of Pb is favorable and sorption of Ni indicates cooperative adsorption and the \(R^2\) value is 0.996 (Pb) and 0.913 (Ni). Cooperative adsorption mechanism of heavy metals is still unclear.

The Temkin isotherm contains a factor explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy). The calculation was carried out by plotting the quantity sorbed \(q_e\) against \(\ln c_e\) and the constants were determined from the slope and intercept. The model is given by the following equation (Temkin et al., 1940):

\[
q_e = \frac{RT}{b} \ln(A_T c_e)
\]

\[
B = \frac{RT}{b}
\]

where \(b\) is Temkin constant related to heat of sorption \((\text{J.mol}^{-1})\), \(A\) is the Temkin isotherm constant \((\text{l.g}^{-1})\), \(R\) is the gas constant \((8.314 \text{ J.mol}^{-1} \text{ K}^{-1})\), and \(T\) is the absolute temperature (K).

The equilibrium data were also applied to the Dubinin–Radushkevich model to determine the type of sorption (physical or chemical) with its mean free energy, \(E\) per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be computed by the following equation:

\[
E = \sqrt[2]{\frac{1}{2BDR}}
\]
where $B_{DR}$ is denoted as the isotherm constant. Meanwhile, the parameter $\varepsilon$ can be correlated as:

$$\varepsilon = RT \ln \left[ 1 + \frac{1}{c_e} \right]$$

(7)

where $R$, $T$ and $c_e$ represent the gas constant ($8.314 \text{ J.mol}^{-1} \text{ K}^{-1}$), absolute temperature (K) and adsorbate equilibrium concentration (mg. l$^{-1}$), respectively. One of the unique features of the Dubinin-Radushkevich isotherm model lies on the fact that it is temperature-dependent; when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed vs the square of potential energy, all suitable data will lie on the same curve, named as the characteristic curve (Hobson, 1969).

Figure 7. Freundlich isotherm model of metals Ni and Pb on magnetically modified orange peel. Determination coefficient of linear regression analysis ($R^2$) – representing the proportion of the dependent variable expressed by the regression line – was used to determine the best corresponding adsorption isotherm.

Table 1. Parameters of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption equation models

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>Isotherm constant</th>
<th>Pb</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_{max}$ (mg/g)</td>
<td>181.818</td>
<td>142.857</td>
</tr>
<tr>
<td></td>
<td>$K_L$</td>
<td>0.010</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.088-0.906</td>
<td>0.478-0.989</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9530</td>
<td>0.1998</td>
</tr>
<tr>
<td></td>
<td>$K_F$ (l/g)</td>
<td>2.103</td>
<td>0.166</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>1.938</td>
<td>0.767</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$l/n$</td>
<td>0.516</td>
<td>1.303</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9964</td>
<td>0.9134</td>
</tr>
<tr>
<td></td>
<td>$b_T$</td>
<td>78</td>
<td>77</td>
</tr>
<tr>
<td>Temkin</td>
<td>$a_T$</td>
<td>0.139</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.8757</td>
<td>0.8744</td>
</tr>
<tr>
<td></td>
<td>$a_D$</td>
<td>88.792</td>
<td>48.429</td>
</tr>
<tr>
<td>Dubinin-Radushkevich</td>
<td>$b_D$</td>
<td>7.301E-07</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.8509</td>
<td>0.8003</td>
</tr>
</tbody>
</table>
**Stability of an adsorbent**

Negligible leaching of iron was observed during sorption experiments. The concentration of iron in solution was determined after sorption and desorption of metal ions. The concentration of iron in solution after sorption and desorption was very low. The adsorbed amount of metal ions was not affected by the loss of iron from magnetic material. This means that the iron oxides are very strongly fixed onto the surface and that the material could be used as Pb and Ni sorbent.

**CONCLUSION**

The magnetically modified orange peel was used to prepare a bio-sorbent the sorption properties of which were studied. The results of experiments show that it is a suitable material for sorption of Pb and Ni ions from water solution. Adsorption data were fitted with linearized form of the Langmuir, Freundlich, Temkin and Dubinin–Radushevich isotherms. The best model describing the biosorption of metal ions on magnetically modified orange peels was the Freundlich isotherm. The results indicate that the adsorption process takes place on heterogeneous adsorbent surface. A better adsorption efficiency was for low concentration of Ni, where efficiency of removal reached 70%. For Pb the efficiency of removal for low concentration of metal ions was 90% and then slowly decreased. At the range of concentrations of 50-100 mg.l\(^{-1}\) the efficiency of removal reached 80%, while for concentration 200 mg.l\(^{-1}\) this value was still 50%. The results of this study indicated that magnetically modified orange peels can be used as low cost, eco-friendly adsorbent for Ni and Pb removal with high efficiency.

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