

Sorption of metals on biological waste material

L. Rozumová¹, P. Kůs¹, I. Šafařík²

¹Research Centre Rez, Hlavní 130, Husinec-Řež, 250 68, Czech Republic
(E-mail: lucia.rozumova@cvrez.cz)

²Department of Nanobiotechnology, Biology Centre, ISB, Na Sadkach 7, Ceske Budejovice, 370 05, Czech Republic

Abstract

Biosorption 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 coffee 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 ($25.2 \text{ mg}\cdot\text{ml}^{-1}$) 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 $0.45 \mu\text{m}$ 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 $5 \text{ g}\cdot\text{l}^{-1}$ of Ni and Pb prepared from chemical reagents of analytical grade: $\text{NiSO}_4\cdot 7 \text{ H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$. 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 $1 \text{ g}\cdot\text{l}^{-1}$ 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 N₂ 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:

$$Removal (\%) = \frac{c_0 - c_e}{c_e} * 100 \quad (1)$$

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:

$$q_e = (c_0 - c_e) * \frac{V}{W} \quad (2)$$

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 m².g⁻¹ and after magnetic modification was increased on 1.60 m².g⁻¹.

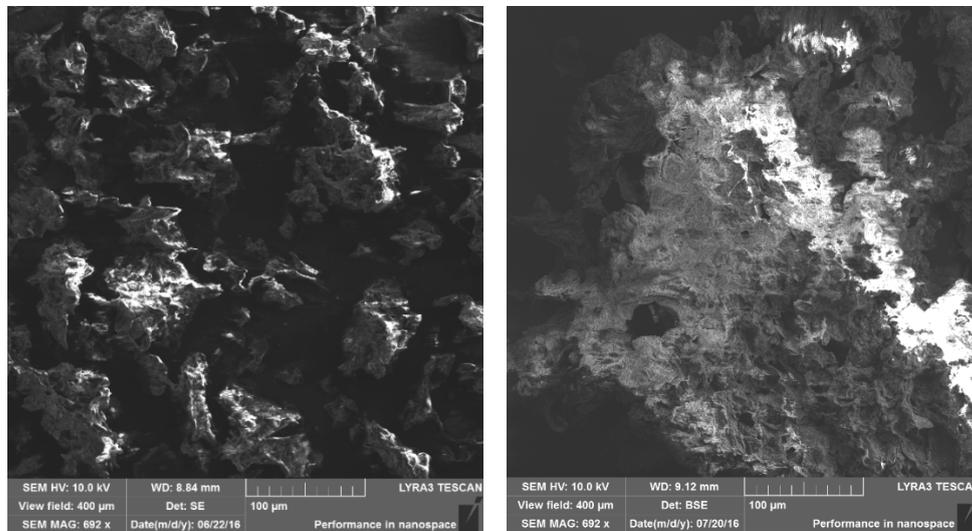


Figure 1. SEM images of magnetically modified orange peels before adsorption of metals (left) and after adsorption of Pb (right).

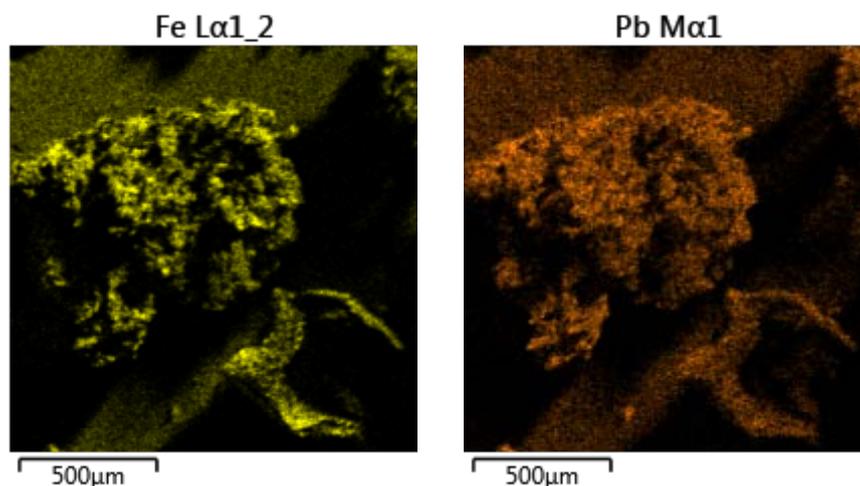


Figure 2. Images of mapping of magnetically modified orange peels after adsorption of metals.

Effect of pH

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.

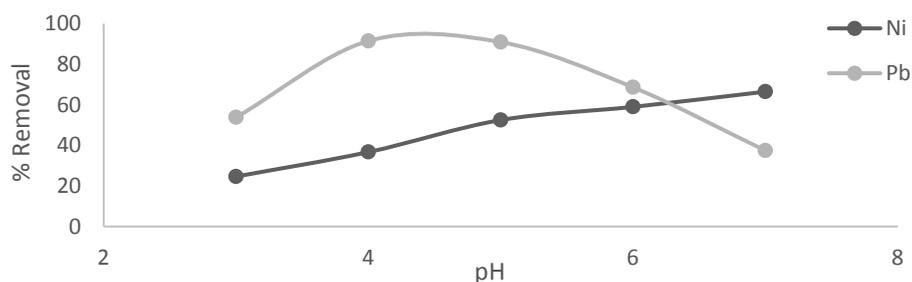


Figure 3. Effect of pH on percentage removal of metals (Ni and Pb) on magnetically modified orange peel.

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.

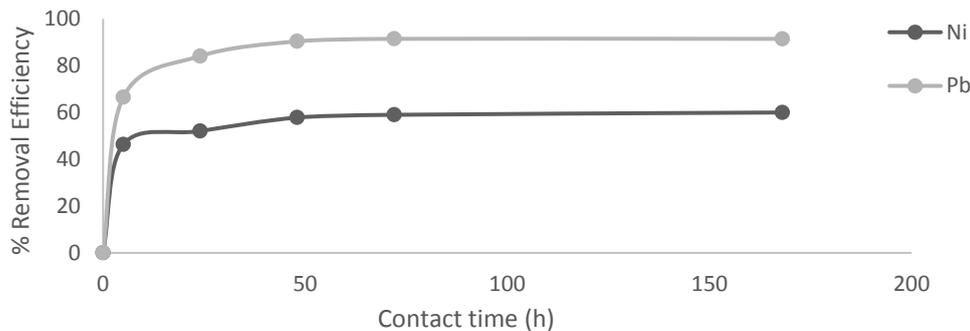


Figure 4. Effect of contact time on percentage removal of metals Ni and Pb on magnetically modified orange peels.

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.

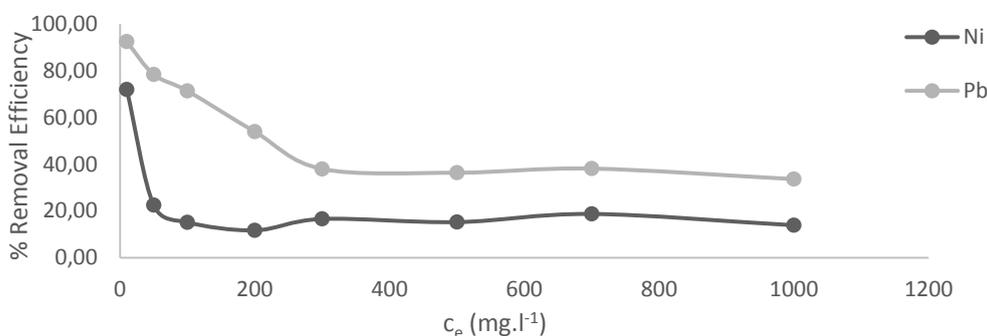


Figure 5. Effect of initial metal concentration on percentage removal of Ni and Pb on magnetically modified orange peels.

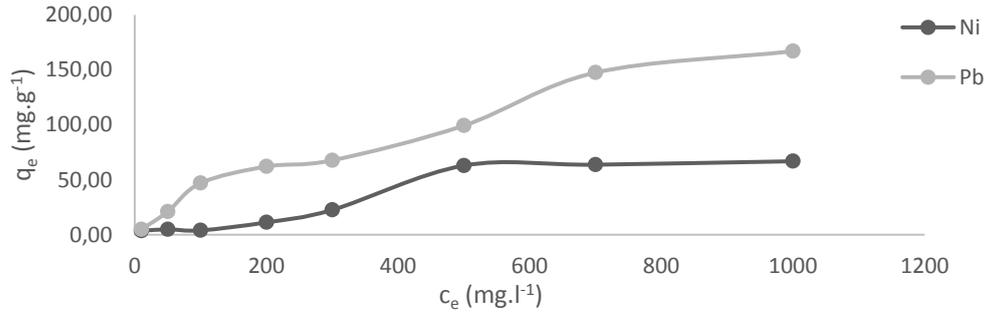


Figure 6. Effect of initial metal concentration on adsorption capacity of Ni and Pb on magnetically modified orange peels.

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):

$$q_e = \frac{q_{max}K_L c_e}{1 + K_L c_e} \quad (1)$$

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 (l/mg). The linearized form of the Langmuir equation is:

$$\frac{c_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{c_e}{q_{max}} \quad (2)$$

The values of q_{max} and K_L were computed from the slope and intercept of the Langmuir plot of $1/c_e$ 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).

$$R_L = \frac{1}{1 + (1 + K_L c_0)} \quad (3)$$

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:

$$q = K_F \cdot c^{1/n} \quad (4)$$

where q (expressed in $\text{mg}\cdot\text{g}^{-1}$) 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):

$$q_e = \frac{RT}{b} \ln(A_T c_e) \quad (5)$$

$$B = \frac{RT}{b}$$

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

The equilibrium data were also applied to the **Dubinín–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:

$$E = \left[\frac{1}{\sqrt{2B_{DR}}} \right] \quad (6)$$

where B_{DR} is denoted as the isotherm constant. Meanwhile, the parameter ε can be correlated as:

$$\varepsilon = RT \ln \left[1 + \frac{1}{c_e} \right] \quad (7)$$

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).

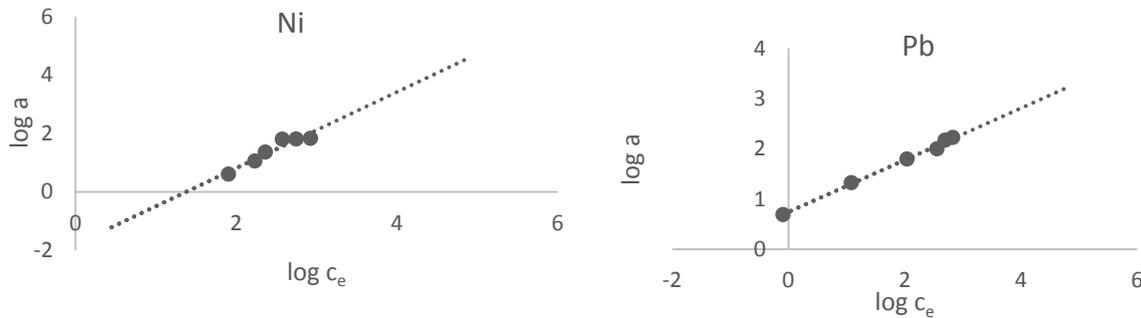


Figure 7. Freundlich isotherm model of metals Ni and Pb on magnetically modified orange peel. Determination coefficient of linear regression analysis (R^2) – representing the proportion of the dependent variable expressed by the regression line – was used to determine the best corresponding adsorption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

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

Isotherm models	Isotherm constant	Pb	Ni
	q_{\max} (mg/g)	181.818	142.857
Langmuir	K_L	0.010	0.001
	R_L	0.088-0.906	0.478-0.989
	R^2	0.9530	0.1998
Freundlich	K_F (l/g)	2.103	0.166
	n	1.938	0.767
	$1/n$	0.516	1.303
	R^2	0.9964	0.9134
	b_T	78	77
Temkin	a_T	0.139	0.012
	R^2	0.8757	0.8744
Dubinin-Radushkevich	a_D	88.792	48.429
	b_D	$7.301\text{E-}07$	0.003
	R^2	0.8509	0.8003

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.

Acknowledgements

Authors thank to the financial support of the Ministry of Education Youth and Sports NPU II Research for SUSEN and Project No. IPNOP 16D0010. This research was also supported by the Grant Agency of the Czech Republic (Project No. 13-13709S).

REFERENCES

- Dada, A.O., Olalekan, A.P., Olatunya, A.M., Dada, O. 2012 Langmuir, Freundlich, Temkin and Dubinin_Radushkevich Isotherms studies of Equilibrium Sorption of Zn²⁺ Unto Phosphoric Acid Modified Rice Husk. *IOSR Journal of Applied Chemistry* **3**(1), 38-45.
- Dubinin, M.M., Zaverina, E.D., Radushevich, L.V. 1947 Sorption and structure of active carbons. *The Journal of Physical Chemistry* **21**, 1351-1362.
- Faostat.org. 2016 Global production of fruits in the world. WWW: <http://faostat3.fao.org/home/E>
- Gohari, M., Hosseini, S.N., Sharifnia, S., Khatami, M. 2013 Enhancement of metal ion adsorption capacity of *Saccharomyces cerevisiae*'s cells by using disruption method. *Journal of the Taiwan Institute of Chemical Engineers* **44**, 637-645.
- Goldberg, S. 2005 Equations and Models Describing Adsorption Processes in Soils. Soil Science Society of America, Segoe Road, Madison, WI 53711, USA. *Chemical Processes in Soils. SSSA Book Series* **8**, 677.
- Grohmann, K., Baldwin, E.A. 1992 hydrolysis of orange peel with pectinase and cellulose enzymes. *Biotechnology Letters* **14**(12), 1169-1174.
- Hobson, J.P. 1969 Physical adsorption isotherms extending from ultra-high vacuum to vapour pressure. *The Journal of Physical Chemistry* **73**, 2720–2727.
- Langmuir, I. 1916 The constitution and fundamental properties of solids and liquids. Part I: Solids. *Journal of the American Chemical Society* **38**, 2221-2295.
- Kiwada, H., Sato, J., Yamada, S., Kato, Y. (1986) Feasibility of magnetic liposomes as a targeting device for drugs. *Chem.*

- Kyzas, G.S., Matis, K.A. 2015 Nanoadsorbents for pollutants removal: a review. *Journal of Molecular Liquids* **203**, 159-168.
- Massart, R.A. 1981 Preparation of aqueous magnetic liquids in alkaline and acidic media. *IEEE Transactions on Magnetics* **17**, 1247-1248.
- Matik, M., Vaclavikova, M., Hredzak, S., Lovas, M., Jakabsky, S. 2004 Úprava odpadových vôd obsahujúcich ťažké kovy použitím magnetických nanočastíc. *Acta Montanistica Slovaca* **9**, 418-422.
- Mockovciakova, A., Orolova, Z., Škvarla J. 2010 Enhancement of the bentonite sorption properties. *Journal of hazardous Materials* **180**, 274-281.
- Oliviera, L.C.A., Rios, R.V.R.A., Fabris, J.D., Sapag, K., Garg, V.K., Lago, R.M. 2003 Clay–iron oxide magnetic composites for the adsorption of contaminants in water. *Applied Clay Science* **22**, 169–177.
- Pourbafrani, M., Forgács, G., Horváth, I.S., Niklasson, C., Taherzadeh, M.J. 2010 Production of biofuels, limonene and pectin from citrus wastes. *Bioresource Technology* **101**(11) 4246–4250.
- Rozumova, L., Zivotsky, O., Seidlerova, j., Motyka, O., Safarik, I., Safarikova, M. 2016 Magnetically modified peanut husks as an effective sorbent of heavy metals. *Journal of Environmental Chemical Engineering* **4**(1) 549-555.
- Safarik, I., Safarikova, M. 2010 Magnetic fluid modified peanut husks as an adsorbent for organic dyes removal. *Physics Procedia* **9**, 274-278.
- Temkin, M.I., Pyzhev, V. 1940 Kinetics of ammonia synthesis on promoted iron catalyst. *Acta Physico-Chimica Sinica* **12**, 327–356.
- Tripodo, M.M., Lanuzza, F., Micali, G., Coppolino, R., Nucita, F. 2004 Citrus waste recovery: a new environmentally friendly procedure to obtain animal feed. *Bioresource Technology* **91**(2) 111-115.
- Voudrias, E., Fytianos, F., Bozani, E. 2002 Sorption Description isotherms of Dyes from aqueous solutions and Waste Waters with Different Sorbent materials. *Global NEST Journal* **4**(1),75-83.
- Widmer, W., Zhou, W., Grohmann, K. 2010 Pretreatment effects on orange processing waste for making ethanol by simultaneous saccharification and fermentation. *Bioresource Technology* **101**(14), 5242-5249.
- Wikandari, R., Nguyen, H., Millati, R., Niklasson, C., Taherzadeh, M.J. 2015 Improvement of Biogas Production from Orange Peel Waste by Leaching of Limonene. *BioMed Research International* 2015, 1-6.