

An Investigation of Langmuir and Freundlich Isotherms for Removing of Pb⁺² ions from Aqueous Solutions by Using Modified Reed

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ABSTRACT

To overcome a drinking water contamination by heavy metals, effective low cost methods for removing heavy metals from aqueous solutions are required. In this study, reed straw was modified by using citric acid at thermal reaction, at different time and different temperatures used to remove Pb⁺² ions from aqueous solutions. The best result for removing Pb⁺² ions was giving at a modification time of 12 h and 120°C. The formation of cellulose _ citric acid cross-linking was confirmed by using FTIR spectrum. The b value of Langmuir isotherm was found to be 6.8 L/mg and q_{max} 45.45 mg/g. The Freundlich constant k_f was 0.91 mg/g and the n value was 3.06.

Keywords: Thermal modification, Langmuir and Freundlich isotherms, Crosslinking

1. INTRODUCTION

Toxic heavy metals contamination is a global concern. These metals exist in aqueous waste streams through a variety of pollution sources, such as mining, refining and electroplating (Gardea-Torresdey et al., 1999). The most common heavy metals in wastewater are copper, cadmium, nickel, cobalt, lead and zinc which are toxic at high concentrations. The heavy metals are not biodegradable and can be carcinogenic if it not fatal at high concentrations (Wartelle, and Marshall, 2000). The rapid industrialization, poor emission control, unorganized urbanization and increase of engine traffic lead to increase the amount of heavy metals, which released into the environment. The plants were affected by heavy metals contamination throughout soil, water, and ambient. The plant roots can absorb these metals from the soil and transport it to leaves, flowers, and seeds (Doganlar, and Atmaca, 2011). Many serious of health hazard such as acute and chronic poisoning can be cause by increasing the level of (Pb⁺²) ion (Hernandez, and Margalida, 2009). The increasing demand for soft water lead to investigate of new low cost materials such as agriculture byproducts as adsorbent for removing of heavy metals from the industrial wastewater (Villaescusa et al., 2004). Conventional methods included chemical precipitation, ion exchange, and adsorption by active carbon used for removing heavy metals from industrial effluent (S.E. Bailey et al., 1999). Most of these methods are suffering from some of drawback such as high capital or high operational cost (Wong et al., 2003). Modified cellulose beads are used recently to remove some of heavy metallic ions (Svoboda, and Canova, 1992). Cellulose materials such as cottonseed hulls, macadamia nuts (Wartelle, and Marshall, 2000), Rice straw (Renminet al ., 2006), soybean straw (Bo et al 2008) and cotton, soybean hulls (Marshall et al., 2001) have been investigated for removing heavy metals from aqueous solutions (Dronnet, et al 1997, Dronnet, et al 1998; Aksu., Isoglu, 2005; Reddad, et al., 2002; Laszlo and Dintzis, 1994). Sorption capacity of agriculture materials can be enhance by treating with poly functional acids such as (citric, tartaric, and phosphoric) at mildly elevated temperature (Wong, et al., 2003), (Marshall, et al., 1999). The present study carried out to determine the adsorption ability of lead by reed material, which was treated with NaOH and citric acid (Marshall et al., 1999; Marshall et al., 2000; Marshall et al., 2001). In addition, to determine the parameters of Freundlich adsorption isotherm and Langmuir adsorption isotherm.

2. MATERIAL AND METHODS

2.1. Materials

Reed straw was collected from Abu-Ghraib area, Baghdad, Iraq. The chemicals provided by Merck, BHD and Fluka companies

2.2 Methods

2.2.1 Adsorbent preparation

The reed straw treated at refluxing with 2% NaOH solution. The treated straw washed and dried in air oven at 50 °C. Dried reed cut into segments of 2-3 mm. Citric acid C.A was subjected to air oven at 50°C until gain constant weight. The reed straw was modified according to method described by Marshall et al, where 0.5 g of treated reed mixed with 1.5 g of citric acid in 8 ml of water and stirred for 30 min at room temperature. The mixed placed in tray dish and dried at 50°C in air oven. The thermo chemical reaction (table 1) between acid and straw proceeded by rising the temperature of the oven 80, 100 and 120°C for 8, 10 and 12h. The best weight (0.63gm) given at 120°C for 12h.

Table-1: The modification conditions of reed straw

Time of reaction h	Temperature of reaction °C	Reed straw(gm)	Weight of C.A (gm) with	Yield of modified reed (gm)
8	80	0.5	0.5	0.49
8	100	0.5	1	0.50
8	120	0.5	1.5	0.54
10	80	0.5	0.5	0.53
10	100	0.5	1	0.54
10	120	0.5	1.5	0.61
12	80	0.5	0.5	0.58
12	100	0.5	1	0.60
12	120	0.5	1.5	0.63

2.2.2 Solution preparations

Solutions of 60, 80 and 100 ppm of lead nitrate were prepared by using deionized water.

2.2.3 Pb^{+2} adsorption experiments

The Adsorption experiment were carried out at PH 6 and room temperature by adding 0.1 gm of modified reed to 50 ml of 100 ppm of lead nitrate solution and shaking in stopper conical flask at 250 rpm for 24 hours. The filtrated solution was subjected to atomic absorption technique. This experiment was repeated for all the other solutions and the results were recorded.

3. RESULTS AND DISCUSSION

The ability of reed straw as ion exchange can be enhanced by subjected it to alkaline media. The treated with dilute NaOH lead to methylated carboxyl's (saponification of ester associated with pectic chain) also to remove some of low molecule weight substances. This process will set off free alcohol groups, which esterified in cellulose molecules. Ultimately, the ability of the cation uptake and the number of alcohol groups, which later esterified with citric acid in thermal reaction stage, will increase. Cellulose enriched with primary alcohol groups was reacted with citric acid. This process lead to further stabilization, due to formation of cross-link between carboxylic groups and different chains of cellulose, which can confirmed by FTIR spectra (figure1).The peak at 2916.37 cm^{-1} belong to (C-H) stretching of alkanes and the peaks at $1041.56 - 1053.13\text{ cm}^{-1}$ are belong to (C-O) group of hydroxyl stretching. Comparing IR spectrum with modified reed straw (figure2) show there is a strong peak at 1722 cm^{-1} belonging to carboxyl group of citric acid. The peak at 1734 cm^{-1} it belong to ester group, which is indicating citric acid esterification. The broad peak around $2914-2895\text{ cm}^{-1}$ indicate the existence of carboxylic groups (OH). The spectrums indicate the existing of modification between citric acid and reed cellulose, which in turn increase the ability of adsorption.

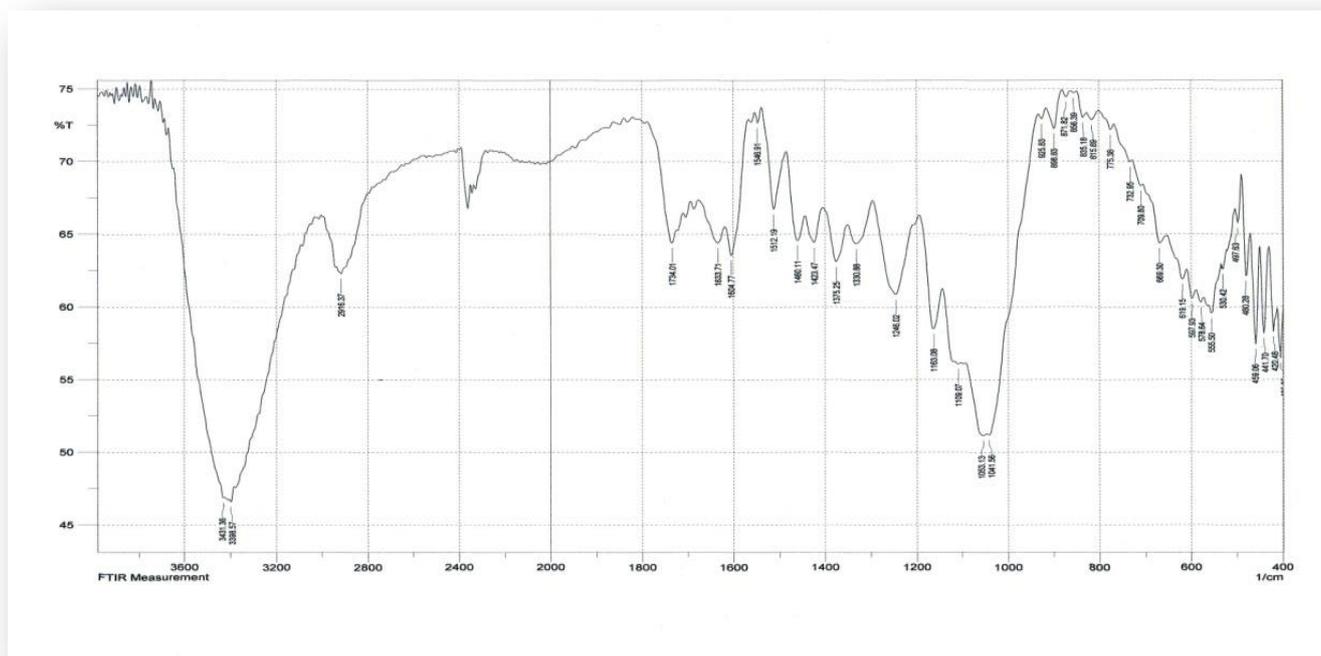


Fig.1: FTIR spectra for reed straw

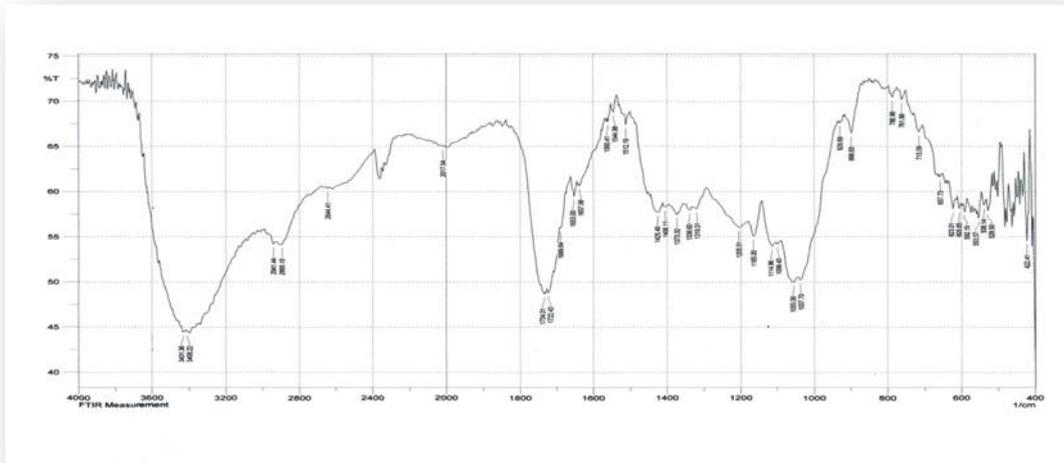


Fig.2: FTIR spectra for reed straw modified with citric acid

4. EFFECT OF INITIAL CONCENTRATION OF Pb⁺² ION

The effect of initial concentration of Pb⁺² ion can be understood in terms of absorption capacity (q_e) which is calculated from the equation

$$q_e = \frac{v(C_i - C_e)}{m}$$

Where, v is the volume of solution in (L). C_i and C_e are the initial and equilibrium concentrations (ppm), m mass of reed straw in gm. When the initial concentration of Pb⁺² ions increase then absorption capacity (q_e) increase. Because, at high concentration the number of ions that may be adsorbed at a particular weight of adsorbent will be higher than the available adsorption sites. However, at high concentration the driving force, i.e. concentration gradient is stronger, and the amount of Pb⁺² ions adsorbed per unit weight of adsorbent are higher. While, at low concentration the number of adsorption sites on the adsorbent will be high, comparing to the ions present in solution, therefore, most of the ions will adsorb at the same weight of adsorbent but the driving force, i.e. concentration gradient is less because of that the absorption capacity will be less.

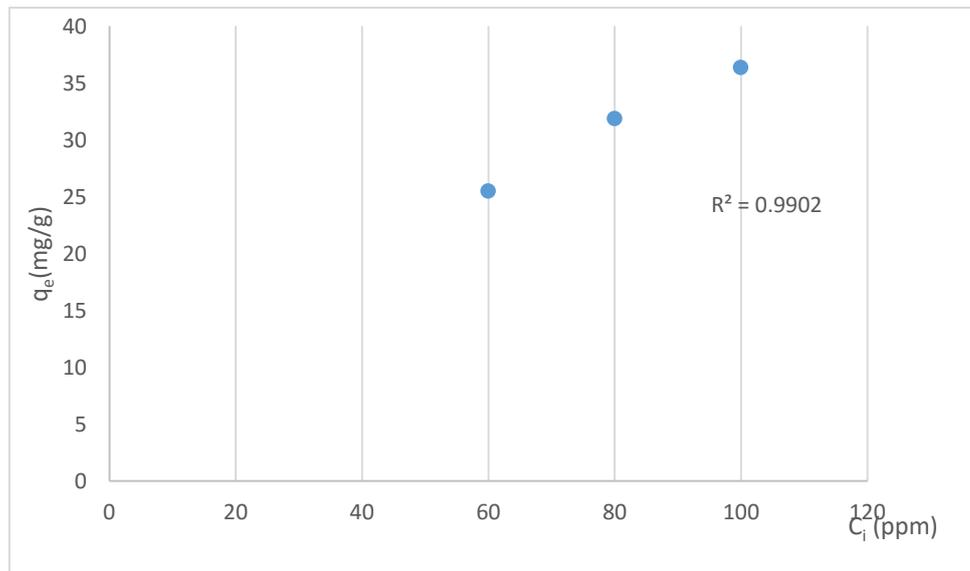


Fig.3: Effect of C_i on q_e of Pb⁺² ion

Table-2: The effect of C_i on q_e for Pb⁺² ion

C_i (ppm)	q_e (mg/g)
100	36.375
80	31.875
60	25.5

5. ADSORPTION ISOTHERM EXPERIMENT

The adsorption isotherm usually described through isotherms, which is the amount of adsorbate on the adsorbent as a function of its pressure (gas) or concentration (liquid) at constant temperature. Several models of isotherm such as Langmuir and Freundlich can describe metal ions distribution between liquid phase and the solid phase (C. Parameswara Murthy, Andra Naidu, 2009; F.Rouquerol, J. Rouquerol and K. Sing, 1999;

C _i of Pb ⁺² (ppm)	C _e of Pb ⁺² (ppm)	Volume (ml)	q _e (mg/g)	$\frac{C_e}{q_e}$	ln (q _e) mg/g	ln(C _e) ppm
100	27.25	50	36.375	0.744	3.59	3.30
80	16.25	50	31.875	0.50	3.46	2.78
60	9	50	25.5	0.35	3.23	2.197

H. Yıldırım Erbil, 2006). The Freundlich adsorption isotherm its purely empirical formula. The linearized of

Freundlich equation can be shown as bellow.

$$\ln q_e = \ln K_f - \frac{1}{n} \ln C_e$$

By applying this equation (table 3).The constants K_f and n can be determined from the plotting between ln q_e and ln c_e (figure 4). Where the value of K_f was (0.91 mg/g) and the value of n was (3.06). The n value represent the degree of nonlinearity between adsorption and solution concentration, (If n=1 the adsorption is linear; if n > 1 the adsorption is physical; if n < 1. The adsorption is chemical). Langmuir assumes that the surface of adsorbent is uniform that is all the adsorption sites are equivalent. At the maximum adsorption only monolayer is formed. Molecules of adsorbate do not deposit on other that is no sorption can take place at the site if it is filled once. This isotherm can be represent by the equation

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}}$$

b and q_{max} constants represented the energy of adsorption and the maximum adsorption capacity respectively. By applying this equation (table 3), these constants can be obtained from the values of slope and intercept, which can determine by plotting $\frac{C_e}{q_e}$ against C_e (figure 5). From the plotting, the value of (b) found to be 6.8 mg/L and q_{max} was 45.45 mg/g.

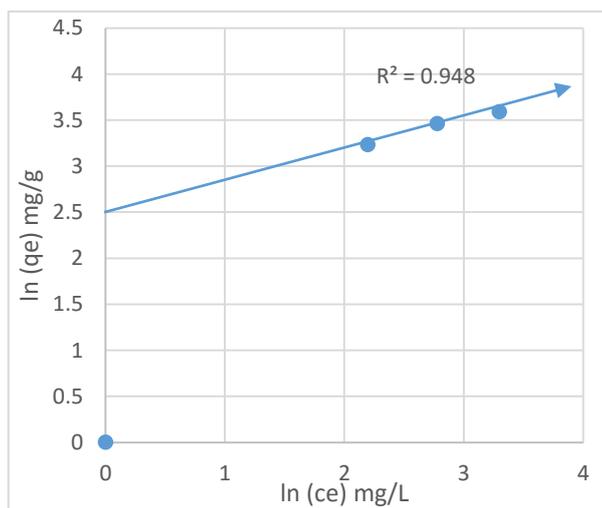


Fig.4: Freundlich isotherm for removing Pb⁺² ions from aqueous solutions

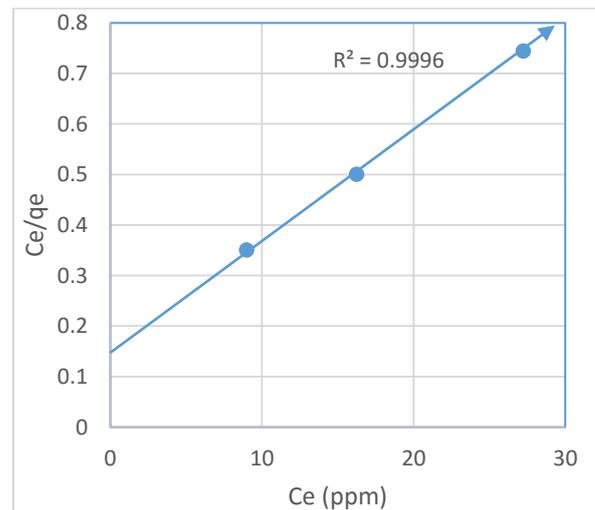


Fig.5: Longmuir isotherm for re moving Pb⁺² ions from aqueous solutions

The essential characteristics of Langmuir are expressed in terms of separation factor R_L (equilibrium parameters) that is a dimensionless constant which given by

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

Where's c_i the initial concentration in mg/L and b is the Langmuir constant the nature of isotherm can indicated from the value of R_L (table 4).

Table-4: the range for R_L values

R_L value	Type of isotherm
$R_L = 1$	unfavorable
$R_L > 1$	linear
$0 < R_L < 1$	favorable
$R_L = 0$	irreversible

The separation factor parameter was calculated and the values were 0.0024, 0.0018 and 0.0014 for the Pb^{+2} ion concentrations 60, 80, and 100 respectively, all these values were between zero and one that indicates the isotherm is favorable.

6. CONCLUSIONS

The present work shows that the best adsorption of Pb^{+2} in aqueous solutions by cellulose modified with citric acid was found at modification temperature of 120°C and time of 12 h. The adsorption is favorable for Langmuir and Freundlich since the values of separation factor R_L of Langmuir isotherm were 0.0024, 0.0018, and 0.0014 and the value of n in Freundlich isotherm was 3.06.

7. REFERENCES

- Aksu, Z. A., Isoglu, Removal of copper (II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp, *Process Biochem.* 40 (2005) 3031–3044, <http://dx.doi.org/10.1016/j.procbio.2005.02.004>.
- Bailey, S. E., Olin, T. J., Brica, R. M., Adrin, D. D., A review of the potential low cost adsorbents for heavy metals, *Water Res.* 33 (1999) 2469–2479, [http://dx.doi.org/10.1016/S0043-1354\(98\)00475-8](http://dx.doi.org/10.1016/S0043-1354(98)00475-8).
- Bo Zhu, Tongxiang Fan, Di Zhang, Absorption of copper ions from aqueous solution by citric acid modified soybean straw, *J. Hazard. Mat.* 153 (2008) 300–308, <http://dx.doi.org/10.1016/j.jhazmat.2007.08.050>.
- Parameswara Murthy, C., Andra Naidu, textbook of engineering chemistry, (2009), p225-228.
- Doganlar, Z. B and Atmaca, M. (2011). "Influence of airborne pollution on Zn,Cd,Cu and Al accumulation and physiological parameters of plant leaves in Antakya (Turkey)," *Water Air Soil poll.* 214(1-4), 509-523, <http://dx.doi.org/10.1007/s11270-010-0442-9>.
- Dronnet, V. M., Renard, C. M. G. C., Axelos, M. A. V., Thibault, J.-F. binding of divalent metal cations by sugar-beet pulp, *Carbohyd. Polym.* 34 (1997) 73–82, [http://dx.doi.org/10.1016/S0144-8617\(97\)00055-6](http://dx.doi.org/10.1016/S0144-8617(97)00055-6).
- Dronnet, V. M., Axelos, M. A. V., Renard, C. M. G. C., Thibault, J.-F. Improvement of the binding capacity of metal cations by sugar-beet pulp. Part 1. Impact of cross-linking treatments on composition, hydration and binding properties, *Carbohyd. Polym.* 35 (1998) 29–37, [http://dx.doi.org/10.1016/S0144-8617\(97\)00118-5](http://dx.doi.org/10.1016/S0144-8617(97)00118-5).
- Dronnet, V. M., Axelos, M. A. V., Renard, C. M. G. C., Thibault, J.-F. Improvement of the binding capacity of metal cations by sugar-beet pulp. Part 2. Binding of divalent metal cations by modified sugar-beet pulp, *Carbohyd. Polym.* 35 (1998) 239–247, [http://dx.doi.org/10.1016/S0144-8617\(97\)00253-1](http://dx.doi.org/10.1016/S0144-8617(97)00253-1).
- Rouquerol, F., Rouquerol, J. and Sing, K. adsorption by powders and porous solids principles, methodology and applications. (1999), P97-98, 112
- Gardea-Torresdey, J. L., Tiemann, K. J., Gamez, G. and Dokken, K. (1999). Effects of Chemical Competition for Multi-metal Binding by *Medicago sativa* (alfalfa). *J.Hazard. Mater.* 69. 41-51, [http://dx.doi.org/10.1016/S0304-3894\(99\)00057-6](http://dx.doi.org/10.1016/S0304-3894(99)00057-6).
- Yıldırım Erbil, H. Surface Chemistry of Solid and Liquid Interfaces, (2006), p 297-300,302
- Hernandez, M., and Margalida, A. "Assessing the risk of lead exposure for the conservation of the endangered Pyrenean bearded vulture (*Gypaetus barbatus*) population," *Environ. Res.* (2009), 109(7), 837-842, <http://dx.doi.org/10.1016/j.envres.2009.05.001>.
- Laszlo, J. A., Dintzis, F. R. Crop residues as ion-exchange materials. Treatment of soybean hull and sugar beet fiber (pulp) with epichlorhydrin to improve cation-exchange capacity and physical stability, *J. Appl. Polym. Sci.* 52 (1994) 531–538, <http://dx.doi.org/10.1002/app.1994.070520408>.
- Marshall, W. E., Wartelle, L. H., Chatters, A. Z., Comparison of attrition in citric acid modified soybean hulls and commercial cation exchange resins, *Ind. Crop. Prod.* 13 (2001), 163–169, [http://dx.doi.org/10.1016/S0926-6690\(00\)00063-7](http://dx.doi.org/10.1016/S0926-6690(00)00063-7).
- Marshall, W. E., Wartelle, L. H., Boler, D. E., Johns, M. M., Toles, C. A., Enhanced metal absorption by soybean hulls modified with citric acid, *Bioresource Technol.* 69 (1999) 263–268, [http://dx.doi.org/10.1016/S0960-8524\(98\)00185-0](http://dx.doi.org/10.1016/S0960-8524(98)00185-0).
- Marshall, W. E., Wartelle, L. H., Boler, D. E., Toles, C. A., Metal ion absorption by soybean hulls modified with citric acid: a comparative study, *Environ. Technol.* 21 (2000), 601–607, <http://dx.doi.org/10.1080/09593332108618075>.

17. Marshall, W. E., Chatters, A. Z., Wartelle, L. H., McAloon, A., Optimization and estimated production cost of a citric acid-modified soybean hull ion exchanger, *Ind. Crop. Prod.* 14 (2001) 191–199, [http://dx.doi.org/10.1016/S0926-6690\(01\)00084-X](http://dx.doi.org/10.1016/S0926-6690(01)00084-X).
18. Reddad, Z. C., Gerente, Y., Andres, M.-C. Ralet Thibault, J.-F., Le Cloirec, P. Ni (II) and Cu(II) binding properties of native and modified sugar beet pulp, *Carbohydr. Polym.* 49 (2002) 23–31, [http://dx.doi.org/10.1016/S0144-8617\(01\)00301-0](http://dx.doi.org/10.1016/S0144-8617(01)00301-0).
19. RenminGong, Youbin Jin, Fayang Chen, Jian Chen, Zhili Liu, Enhanced malachite green removal from aqueous solution by citric acid modified rice straw, *J. Hazard. Mat.* B137 (2006) 865–870, <http://dx.doi.org/10.1016/j.jhazmat.2006.03.010>.
20. Svoboda, L. Canova, Sorption of lead and cadmium on Ostsorb P and Ostsorb SA-5 cellulose sorbents, *Collect. Czech. Chem. Commun.* 57 (1992), 2089, <http://dx.doi.org/10.1135/cccc19922089>.
21. Vaughan, T. C. W., Seo, W. E., Marshall, Removal of selected metal ions from aqueous solution using modified corncobs, *Bioresour. Technol.* 78 (2001), 133–139, [http://dx.doi.org/10.1016/S0960-8524\(01\)00007-4](http://dx.doi.org/10.1016/S0960-8524(01)00007-4).
22. Villaescusa, I., Fiol, N., Martinez, M., Miralles, N., Poch, J., Serarols, J. Removal of copper and nickel ions from aqueous solutions by grape stalks wastes, *Water Res.* 38 (2004), 992–1002, <http://dx.doi.org/10.1016/j.watres.2003.10.040>.
23. Wafwoyo, W., Seo, C. W., Marshall, W. E., Utilization of peanut shells as adsorbents for selected metals, *J. Chem. Technol. Biotechnol.* 74 (1999), 1117–1121, [http://dx.doi.org/10.1002/\(SICI\)1097-4660\(199911\)74:11<1117::AID-JCTB151>3.0.CO;2-R](http://dx.doi.org/10.1002/(SICI)1097-4660(199911)74:11<1117::AID-JCTB151>3.0.CO;2-R).
24. Wartelle, L. H. and Marshall, W. E. 2000. Citric Acid Modified Agricultural By-products as Copper Ion Adsorbents. *Adv. Environ. Res.*, 4: 1-7, [http://dx.doi.org/10.1016/S1093-0191\(00\)00002-2](http://dx.doi.org/10.1016/S1093-0191(00)00002-2).
25. Wartelle, L. H., Marshall, W. E., Citric acid modified agricultural by-products as copper ion adsorbents, *Advances in Environmental Research* 4 (2000), 1–7, [http://dx.doi.org/10.1016/S1093-0191\(00\)00002-2](http://dx.doi.org/10.1016/S1093-0191(00)00002-2).
26. Wong, K. K., Lee, C. K., Low, K.S., Haron, M. J., Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions, *Chemosphere* 50 (2003), 23–28, [http://dx.doi.org/10.1016/S0045-6535\(02\)00598-2](http://dx.doi.org/10.1016/S0045-6535(02)00598-2).
27. Wong, K. K., Lee, C. K., Low, K. S., Haron, M. J., Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk, *Process Biochem.* 39 (2003), 437–445, [http://dx.doi.org/10.1016/S0032-9592\(03\)00094-3](http://dx.doi.org/10.1016/S0032-9592(03)00094-3).