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ADSORPTION CAPACITIES OF DIFFERENT LIGNOCELLULOSIC MATERIALS FOR COPPER IONS

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Abstract: *Different lignocellulosic waste materials was able to sorb heavy metal ions, and other polutants, for example dyes, from aqueous solutions. In this study the efficiencies of adsorption of copper ions from water by poplar wood sawdust and sugar beet pulp were investigated. Adsorption experiments were performed at room temperature, with four different biosorbent doses of 2.5 g/l, 5 g/l, 10 g/l and 15 g/l, which were added in the model water with different initial copper ion concentration from 10 mg/l to 250 mg/l. The initial pH of model water was 4 and contact time of model water and the biosorbent was 90 min. The sugar beet pulp is shown as better adsorbent for copper ions than poplar wood sawdust. The adsorption were considered by the Langmuir and the Freundlich adsorption model. The results demonstrate that the efficiency of copper ions removal from the water is better at higher dose of adsorbent, but maximal adsorption capacities have to be estimate with lower doses of adsorbent. Langmuir adsorption isotherm better describes the adsorption of copper ions than Freundlich adsorption isotherm. This means that the surfaces of both investigated adsorbents are homogeneous, i.e. with the same active sites for adsorption of copper ions.*
Keywords: *adsorption, copper, sugar beet shreds, poplar wood sawdust*

1. INTRODUCTION

Considering the harmful effects of heavy metals, it is necessary to remove them from liquid wastes at least to a limit accepted by national and international regulatory agencies. There are many processes that can be used for heavy metal ions removal from water and wastewaters. One of them is biosorption, adsorption by different materials of organic nature, which should be renewable and low-cost.

Various waste microorganisms (Arief et al., 2008; Wang and Chen, 2009), forestry and agroindustrial wastes (Sciban and Klasnja, 2004; Johnson et al., 2008) and natural polymers (Son et al., 2004; O´Connell et al., 2008; Guo et al., 2008; Klimaviciute et al., 2010) can be used as efficient biosorbents. The efficiency of the adsorption of heavy metal ions by some solid adsorbent is dependent on a number of parameters: the amount of the adsorbent, the adsorbent surface area and porosity, the concentration of adsorbate, initial pH of water, contact time of the adsorbent and water, temperature, the presence of competitive ions, etc.

The first and most important step in testing of new biosorbents is to determine their adsorption capacity. For determination of adsorption capacity and explanation of the adsorption process at equilibrium conditions, the adsorption isotherms are used (Foo and Hameed, 2010). They are the most appropriate method in designing and assessing the performance of the adsorption systems.

In this paper, the influence of biosorbent doses on values of adsorption constants in adsorption models, are considered. It was investigated adsorption of copper ions by two biosorbents, poplar wood sawdust and sugar beet pulp, from metal ion solutions of different concentrations. The obtained results are fitted with Langmuir and Freundlich, two, the most common adsorption isotherms.

2. MATERIALS and METHODS

2.1. Materials

Dry sugar beet shreds, from one local sugar factory, were milling on Miag laboratory cone mill. Milled sugar beet shreds and poplar wood sawdust were sieved on the Bühler laboratory sifter (gyratory in a horizontal plane), model MLU-300. Part of the stock having particles in the range 224-400 μm was used in adsorption experiments. Specific surface areas of sugar beet shreds and poplar wood sawdust were 0.80 and 1.05 m^2/g, respectively, which obtained via low-temperature nitrogen adsorption measurements (Micrometrics, ASAP 2000).

Model waters with different initial copper ion concentrations from 10 mg/l to 250 mg/l, was prepared by dilution of stock solutions with demineralised water. The stock solution of copper (0.25 mol/l) were prepared by dissolving of certain amount of $CuSO_4 \cdot 5H_2O$ in demineralised water. pH in model water was adjusted to 4, by adding 0.5 mol/l acetic acid, in accordance with previous investigations (Šćiban and Klašnja, 2004). All chemicals used were of analytical reagent grade.

2.2. Adsorption experiments

Batch adsorption experiments were carried out by shaking of 5 g of biosorbent with 1 litre of model water, from 3 hours, in accordance with previous investigations (Šćiban and Klašnja, 2004). After that, the biosorbent was removed from water by vacuum filtration through Gooch G3 crucible. Concentrations of metal ions before (C_o) and after adsorption (C) were determined komplexometrically (Sajo, 1973). On the base of the measured values, adsorption efficiency (E) and amount of adsorbed metal ions per specified amount of adsorbent (q) can be calculated:

$$E\ (\%) = ((C_o - C)/C_o) \cdot 100 \quad (1)$$

$$q = (C_o - C)/m \quad (2)$$

where m is the amount of adsorbent per litre of model water.

To determine the adsorption capacity of investigated adsorbents, the Langmuir (3) and the Freundlich (4) adsorption models were used:

$$q = (q_m \cdot K_L \cdot C)/(1 + K_L \cdot C) \quad (3)$$

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

where q is the amount of ions adsorbed per specified amount of adsorbent in equilibrium, C the ions equilibrium concentration, q_m the Langmuir constant which represent the amount of ions required to form a monolayer on the adsorbent surface, K_L the Langmuir equilibrium constant related with the enthalpy of adsorption, and K_F and n the Freundlich equilibrium constants.

Langmuir adsorption isotherm refers to homogeneous adsorption, which each adsorbate possess constant enthalpies and adsorption activation energy (all adsorption sites possess equal affinity for the adsorbate), with no transmigration of the adsorbate in the plane of the adsorbent surface. Freundlich isotherm is the earliest known, empirical model,with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface.

Computer simulation technique was applied to fit the linear form of Langmuir and Freundlich equations for the adsorption data. The goodness of fit of investigated adsorption models was estimated by coefficients of determination (R^2).

3. RESULTS and DISCUSSION

The adsorption capacities of sugar beet shreds and poplar wood sawdust for copper ions were determined by constructing the corresponding equilibrium isotherms (Figs 1 and 2).

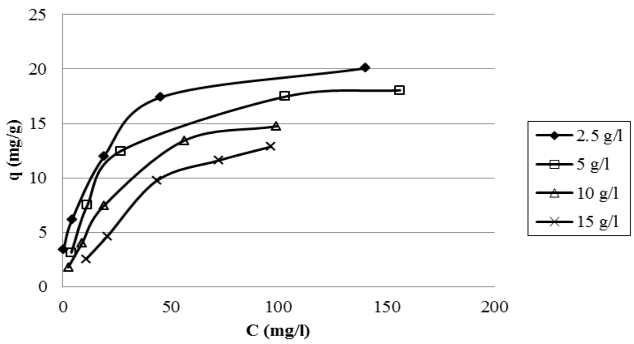

Figure 1. Adsorption isotherms of Cu(II) ions adsorption onto sugar beet shreds

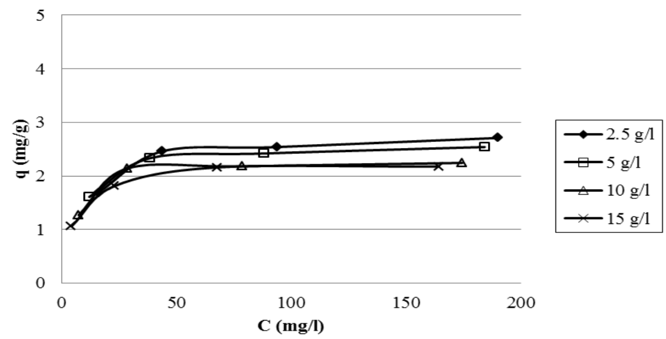

Figure 2. Adsorption isotherms of Cu(II) ions adsorption onto poplar wood sawdust

Figs. 1 and 2 show that the copper ions adsorption per unit mass of biosorbent (q) increased as the biosorbent concentration decreased. On the other hand with the smaller amount of biosorbent the lower adsorption efficiency (E) is achieved, what is direct result of smaller available surface area. Also, the results show that the adsorption of copper ions is better by sugar beet shreds than by poplar wood sawdust, esspecially from the solutions with higher concentration of copper ions.

According to the shape of isotherms, it can be concluded that the adsorption on these two biosorbents is quite different. The reason for this phenomenon is probably their different chemical composition. Specifically, the sugar beet shreds contain much more pectin and less lignin than sawdust of any wood, and consequently have different kinds and position of adsorption sites.

On the base of presented results, the constants in Langmuir and Freundlich adsorption isotherms are calculated and presented in Tables 1 and 2.

Table 1. Constants in Langmuir and Freunlich adsorption isotherms for adsorption of copper ions by sugar beet shreds

m (g/l)	q_m (mg/g)	K_a (l/mg)	R^2	K_f	n	R^2
2.5	21.19	0.110	0.993	4.56	3.24	0.974
5	19.57	0.075	0.987	2.08	2.16	0.919
10	19.34	0.034	0.990	1.09	1.67	0.979
15	26.11	0.011	0.912	0.74	1.58	0.971

Table 2. Constants in Langmuir and Freunlich adsorption isotherms for adsorption of copper ions by poplar wood sawdust

m (g/l)	q_m (mg/g)	K_a (l/mg)	R^2	K_f	n	R^2
2.5	2.86	0.105	0.999	1.093	0.183	0.843
5	2.61	0.147	0.999	1.146	0.163	0.842
10	2.29	0.236	0.999	0.998	0.175	0.768
15	2.22	0.223	0.999	0.853	0.204	0.900

It is evident from the results presented in Tables 1 and 2 that maximum capacity (q_m) of sugar beet pulp is almost ten times larger than capacity of poplar wood sawdust, and in general, than capacities of sawdust of any kind of wood (Sciban and Klasnja, 2004; Low et al., 2004; Božić et al., 2009) or wood bark (Aoyama et al., 1993; Seki et al., 1997). As expected, increase in biosorbent quantity results in maximal capacity decrease.

An exception is the increased adsorption capacity of sugar beet shreds when it is appled in quantity of 15 g/l. Fig. 1 shows that the curve for the 15 g/l is not yet reached plateau, and this results in increased adsorption capacity for this case. The conclusion of these consideration would be that the investigation of adsorption efficiency of some biosorbent should be done with higher adsorbent dose, and determination of maximal adsorbent capacity with lower adsorbent dose.

If it is compared the coeficients of determination (R^2) it can be seen that the Langmuir adsorption isotherm better describes adsorption both at sugar beet shreds and poplar wood sawdust, than Freundlich adsorption isotherm. In that case, the assumption is that the surface of both biosorbents are homogenous, i.e. all active sites for the adsorption are of the same type, although these complex biomaterials have got a few different functional groups. This is the case with many other raw biosorbents, for example different types of wood (Sciban and Klasnja, 2004; Rafatullah et al., 2010), peanut hulls (Brown et al., 2000), hazelnut shell (Cimino et al., 2000) etc. However, this is not the general case, because for adsorption by papaya wood (Basha et al., 2008), mustard oil cake (Ajmal et al., 2005) etc. it was established the similar fit both for Langmuir and Freundlich adsorption isotherms, with experimental results.

4. CONCLUSIONS

In this study the efficiency of adsorption of copper ions from water by sugar beet pulp and poplar wood sawdust was investigated. Adsorption experiments were performed at room temperature with four different biosorbent doses of 2.5 g/l, 5 g/l, 10 g/l and 15 g/l, which were added in the model water with the different initial copper ion concentration. The contact time of model water and the biosorbent was 90 min. The adsorption constants were determined by the Langmuir and the Freundlich adsorption model.

Considering adsorption capacity, the sugar beet shreds are better biosorbent than poplar wood sawdust. The results demonstrate that the efficiency of copper ions removal from the water was better at higher dose of adsorbent, and at low metal ion concentrations. On the other hand, adsorption capacity should be determine by using lower adsorbent dose. Langmuir adsorption isotherm better describes the adsorption of copper *ions than Freundlich adsorption isotherm, and that means the surface of investigated biosorbents are homogeneous, with the same active sites for the copper ions adsorption.*

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