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Utilization of agricultural and industrial wastes for metal removal from aqueous solutions

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In this study a possibility of obtaining sorbents from basketry wastes has been investigated. Therefore, adsorption of cadmium ions on wicker bark of *Salix americana* has been studied. The obtained experimental results were described by the Freundlich equation and adsorption kinetics by the pseudo-second order equation. The effect of pH on cadmium ions adsorption by *S. americana* was also investigated. It has been found that for the pH values ranging from 2 to 7 cadmium removal from the solution was held at almost constant level.

Keywords: waste, adsorption, heavy metals, toxicity, wicker bark, Freundlich isotherm, kinetic.

INTRODUCTION

The society of the turn of the XXth and XXIst century is typified by mass production, huge amounts of consumption and waste, excessive exploitation of limited fossil fuels (coal and petroleum)[1]. This in consequence leads to global environment pollution, which includes soil, air and water. Many industrial wastewaters such as metallurgical, chemical manufacturing, mining, battery manufacturing industries, metal plating facilities and tannery contain high concentrations of toxic heavy metals[2, 3]. Their harmful effects on many forms of life are well known. Metals significantly toxic to human beings and ecological environments include lead, cadmium, copper, mercury and zinc[4].

Among methods used for waste water treatment are chemical precipitation, ion exchange, reverse osmosis, coagulation, membrane separation and adsorption[5, 6]. Despite their efficiency they have some drawbacks, including high operating costs (ion exchanger, active carbon), large volumes of sludge or difficulties with recycling and reuse of adsorbents and ion exchangers[5, 6, 7]. Adsorption technique is considered to be amongst the most favorable processes because of its high efficiency and complete removal of metal ions even at low concentrations[5]. Cost effective technologies or sorbents for treatment of metals contaminated waste streams are needed. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents[8]. Agricultural materials contain e.g. proteins, polysaccharides and lignin which are associated with functional groups responsible for metal ion adsorption. The abundant natural occurrence and presence of large amount of surface functional groups make various agricultural wastes good alternatives to expensive synthetic adsorbents[5]. Some of the reported low-cost sorbents include bark and tannin-rich materials, lignin, chitin, dead biomass, seaweed, zeolite and fly ash[8].

In this work adsorption of cadmium ions on wicker bark of *Salix americana* has been studied. This material contains i.a. phenolic substances – mainly salicin, tannins, dyes, approximately 20 – 45% lignin and phlobaphens and 10 – 35% cellulose and hemicellulose[9]. These substances and their derivatives are known for good extraction and adsorption properties.

According to Central Statistical Office crop area of wicker in Poland in 2009 amounted to ca. 5868 ha[10], and ca. 75% accounted for *S. americana* plantations. It is because of its easy cultivation and decortication (gentrification)[11]. On average one gets ca. 3.5 t of wicker from 1 ha, which in turn from 1t gives 20 – 25% of bark (waste).

EXPERIMENTAL

Materials

Wicker bark of *Salix americana* was commissioned by planters from the county of Nowy Tomyśl. Bark fibers were dried in a Binder laboratory dryer at 100°C until constant mass was obtained. It was then kept in a dessicator before grinding. The bark was then sieved and only the particles that passed through a 70 mesh were used for further analysis.

In all experiments deionized water was used.

Experimental analysis

Batch adsorption tests were carried out at room temperature by taking together ca. 1 g of bark and portion of $CdCl_2$ test solution containing 55 mgCd/dm^3 at pH value ca. 4.0 in a stoppered flask. The flask was then shaken in a shaker until equilibrium was reached.

The mixture was then centrifuged for 15 minutes at 4000 rpm and the solution was taken for the metal ion concentration analysis by means of F-AAS. The effect of shaking time was checked at least in duplicate. Different solutions were sampled by varying the shaking time.

The effect of pH on cadmium ions adsorption by wicker bark was carried out likewise. However, pH values ranged from 2.0 to 7.0, the initial metal ion concentration was 20 mgCd/dm^3 and the flasks were shaken for 120 minutes.

The relative errors of the analytical methods were as follows: determination of pH less than 1%, AAS analysis of cadmium(II) less than 5%.

RESULTS AND DISCUSSION

The experiments of Cd(II) adsorption kinetics from test solutions enabled to determine the time needed to reach equilibrium. The amount of adsorbed cadmium ions as a function of time is shown in Figure 1. The percentage sorption of the metal defined as the ratio of decrease in metal concentration after the adsorption (C_o-C_t) to the initial concentration in aqueous solution (C_o), was calculated according to equation[12]:

$$A\% = \frac{C_o - C_t}{C_o}100 \quad (1)$$

The obtained results show that after 1 hour of shaking the % adsorption $q_{t(60)}$ amounted to 93% and decreased to 90% in the next hours of the contact time. This unusual behavior may be linked to leaching of coloured organic compounds existing in the bark, which probably react with cadmium(II). Moreover, the BET surface area of the bark was 1.301 m^2/g, which allows to make an assumption that wicker bark is a nonporous material. The data shown in Figure 1 were then used to define the adsorption kinetics. They were regressed against a pseudo-first-order kinetic equation and against a pseudo-second-order equation. The metal uptake per unit weight of bark q_e (mg/g) at equilibrium and the rate constant of the pseudo-second-order kinetics equation k were calculated from the equation[2]:

$$(t/q_t) = (1/[kq_e^2]) + (1/q_e)t \quad (2)$$

where:

q_e – metal uptake per unit weight of adsorbent at equilibrium [mg/g],

q_t – metal uptake per unit weight of adsorbent at time t [mg/g],

k – rate constant of the pseudo-second-order kinetics equation [g/mg min].

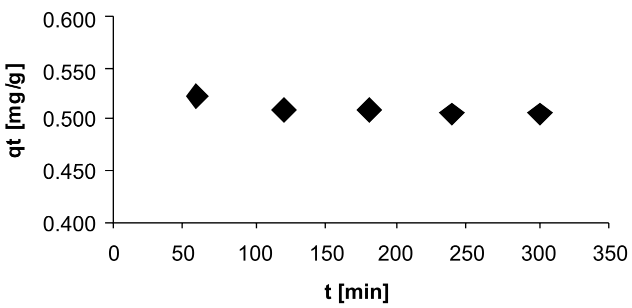

Figure 1. Amount of adsorbed Cd(II) ions as a function of time

The rate constant of the pseudo-second-order kinetics equation k = -0.224 g/mg·min and metal uptake per unit weight of bark at equilibrium was 0.523 and 0.503 mg/g (experimental and calculated value, respectively). In addition, percent difference of exp and cal values of Cd(II) uptake Δq_e = 3.67% and square correlation coefficient R^2 = 1.0.

The obtained equilibrium data were analyzed in the light of Langmuir and Freundlich isotherms. The Freundlich constants were calculated from the linearized form of the equation[4]:

$$\log x/m = \log K + 1/n \log C_e \quad (3)$$

where:

x/m – amount of metal ions adsorbed per unit mass of adsorbent [mg/g],

C_e – equilibrium concentration of heavy metal ions [mg/dm^3],

K,n – the Freundlich constants.

Freundlich constants were -0.31 and 0.98 for K and n, respectively with square correlation coefficient R^2 = 0.9931. Meena et al.[4] suggested that the adsorption behavior of Cd(II) on mustard husk is in good agreement with Langmuir model with constants q_e, b, R^2 and R_L 42.85 mg/g, 0.28 l/mg, 0.9955 and 0.26, respectively. However, R^2 = 0.9927 for Freundlich isotherm and K and n constants were 1.62 and 2.63, respectively.

The next step of the experiment was to determine the effect of pH values on cadmium ions adsorption on wicker bark. As Cd(II) can precipitate from solutions with pH values higher than 7.0, these were not investigated. Figure 2 shows the experimental data of adsorption as a function of pH. In the analyzed pH range % adsorption amounted to 84% to 91%, while Guo et al.[13] observed an increase of cadmium ions adsorption in a narrow pH range from 2.0 to 5.0, further increasing the pH resulted in smaller adsorption increase. At pH 4.0 less than 27% of Cd(II) was adsorbed by lignin from black liquor . On the other hand, Meena et al.[4] obtained 70% adsorption at pH 4.0.

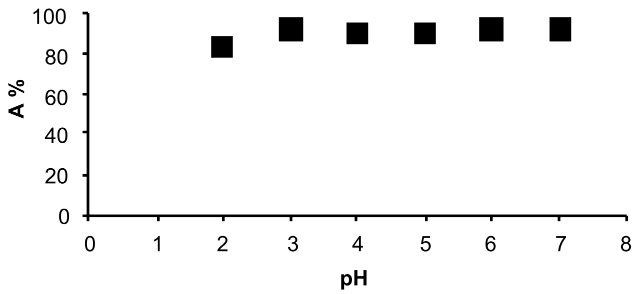

Figure 2. Effect of pH on Cd(II) adsorption on wicker bark

CONCLUSIONS

Adsorption of cadmium ions on wicker bark appears to follow the pseudo-second-order reaction kinetics with the highest efficiency achieved within the first hour of contact time ($q_{t(60)}$ 93%). The rate constant k = -0.224 g/mg·min and the experimental value of metal uptake per unit weight of bark at equilibrium (0.523 mg/g) was slightly higher than the calculated one (0.503 mg/g).

The experimental data were in good agreement with the Freundlich isotherm and equation constants K and n amounted to -0.31 and 0.98, respectively.

The pH reaction had little affect on percent adsorption of Cd(II) on wicker bark. This suggests that bark may adsorb cadmium ions in a relatively wide pH range.

The textural characterization of bark was investigated by N_2 adsorption at 77 K and on that basis BET surface area was calculated (1,301 m^2/g). Poplar sawdust (1.05 m^2/g) had similar surface area[14]. Whereas in Teles de Vasconcelos et al.[15] work adsorption surface area of natural pine bark was 0.317 m^2/g.

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