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Comparative study on heavy metal removal from industrial effluents by various separation methods

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ABSTRACT

Removal of heavy metal ions from industrial effluents can be carried out by various separation processes. In this work the aims were (i) to manufacture ion exchange particles from lignocellulotic materials formed as a waste in bio-processes, like biodiesel production from rapeseed; (ii) to apply these particles for copper ions removal and (iii) to compare the effectiveness of the process with different separation techniques: adsorption with chelating and complexation-ultrafiltation method. In our laboratory ion exchange materials based on lignocellulosic substances was planned to prepare and study. Our aims was to convert the macromolecules of starch- and cellulose-containing materials with the intake of different ionic groups according to the guidelines of the 'green' chemistry into polyelectrolytes, which have an adsorptive and ion-exchange capacity much higher than that of the original matrix.

Keywords: ion exchange; adsorption; ultrafiltration; biobased; rapeseed; agro-waste; water treatment

1. Introduction

Some of the industrial effluents – especially from the environmental polluting chemical technologies – contain significant quantity of toxic contamination, heavy metals, organic dies, etc, which could have a harmful effect on recipient sewage works, too. These effluents should be treated and the hazardous compounds have to be separated. Regarding heavy metals, various methods have been used for their removal, including chemical precipitation, neutralization, membrane filtration, and adsorption [1–3].

The strict regulation for environmental protection in industrial areas means a strong motivation to develop environmental-safe, cost effective technologies for water treatment. At the same time there is a high demand for the alternative utilisation of agro-wastes. The solution for both cases might be to use the derivatives of agro-wastes in water treatment processes as adsorbents or ion exchange materials.

It is well-known that cellulolytic agro-wastes possess a natural ion exchange capacity [4]. Recently numerous products from agro-wastes like peanut hull pellet, banana pith, wheat shell, wheat bran were studied [5–8]. Their advantage over the petro chemical resins is that they can be biologically degraded and the price is lower. Their wider utilisation, however, hinders highly the lack of correct information on capacity, selectivity, chemical resistance etc. Therefore finding of potential raw materials, agro-wastes and their conversion into value-added products, moreover determination of products features are one of the most important research areas nowadays.

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To improve the physico-chemical character and sorption capacity of certain agro-wastes various chemical modifications can be applied. Among them thermo-chemical reaction with citric acid is widely used.

The scheme of the reaction can be seen in Fig. 1. The thermo-chemical reaction between the polysaccharides and citric acid results in citrates; and these citrate derivatives have good ion exchanging attributes.

The effect of heat results in a condensation product, citric acid anhydride. The reactive anhydride is combined with starch or cellulosic hydroxyl groups to form an ester linkage and introduce carboxyl groups to the starch or corn fiber. The addition of the carboxyl functions increased binding with positively charged metal ions [9–11].

Numerous raw materials are studied word wide, e.g., mainly soybean hull and corn fiber in the U.S.A., rice hull and wheat straw in Asia [9,12–16]. We have chosen another agro-waste: it is rape seed pellet or RP cellulose. RP cellulose is derived from the biodiesel production, as a lignocellulosic agricultural waste material. The RP cellulose is a cake residue of rape seed, after pressing the oil from it (which is converted into biodiesel by a transesterification reaction). It contains mainly cellulose, hemicellulose, lignin, protein and triglyceride.

In our experimental work RP cellulose citrate was manufactured from RP cellulose by citric acid reaction. The product has ion exchange capacity. The RP cellulose ion exchange material was used for the removal of heavy metals, including copper, and in this paper the efficiency was compared with two other methods, a polymer enhanced ultrafiltration and adsorption with chelating technique. Ultrafiltration is a widely used membrane process, but alone it is not suitable for metal ion removal [17,18]. The use of water-soluble metal-binding polymers in combination with UF is a hybrid approach to concentrate selectively and to recover valuable elements as heavy metals. In the complexation–UF process cationic forms of heavy metals are first complexed by a macroligand in order to increase their molecular weight with a size larger than the pores of the selected membrane that can be retained whereas permeate water is then purified from the heavy metals [19]. The chelating polymeric ligands are characterized by the reactive functional groups containing O, N, S, or P as donor atoms, and they are capable of forming a coordination complex with different metal ions [20].

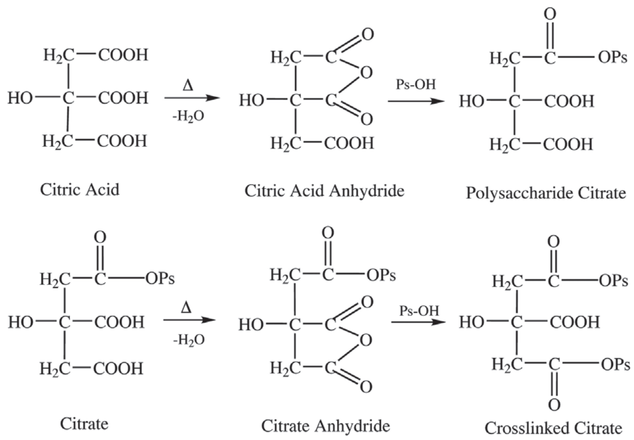

Fig. 1. Thermo-chemical reaction of polysaccharides and citric acid.

2. Materials and methods

For the ion exchange experiments RP cellulose is purchased from Öko-Line Hungary Kft (Hungary), the Solka Floc BW200 microcrystalline lignin-free pure cellulose is from Brown Co (USA). Citric acid and other chemicals are provided by Spektrum 3D Kft (Hungary). All of the chemicals were reagent grade.

A cationic sorbent was prepared from RP cellulose and citric acid using the solid phase esterifying technique (the scheme is shown in Fig. 2). In laboratory scale citric acid solution was mixed with powdered RP

Fig. 2. Scheme of cellulose citrate preparation.

cellulose, providing the rate RP cellulose: citric acid 1:2. The mixture was dried at 35°C until the weight became constant, resulting a hard, bulky material, which was then ground and sieved to provide the suitable particle size, which means greater contact surface for the thermo-chemical reaction. Then the sample was placed in an oven to dehydrate at 60°C for 24 h. That way all surface moisture has been removed and the RP cellulose particles were reacted with citric acid. Oven temperature was adjusted to 145°C for 40 min. The resulting material was washed with distilled water until the pH of the suspension became neutral, filtered and dried at room temperature.

Copper (Cu) removal from aqueous solution with modified RP cellulose was investigated to evaluate its capacity of cation exchange. The effects of various experimental parameters (solution pH, contact time, particle size) were studied in batch reactions.

For the binding experiments $CuSO_4$ solution of 5.5 g/l concentration was employed, which was prepared from analytical grade mineral water-free $CuSO_4$. The samples were stirred with a magnetic stirrer in the copper solution for 1 h to reach intensive contacting.

During the binding process, pH value decreases, the solution is getting more acidic, due to the H^+ ions deriving from the ion exchange. Therefore, to reach the suitable copper binding capacity, it was needed to monitor and control the pH value of the solution (by NaOH) during the measurements. After an hour the solution was filtered and the Cu content of filtrate was titrated complexometric with EDTA solution in presence of murexide indicator.

The experiments were carried out several times and the binding without sorbent was investigated to ensure, that it was caused by the RP cellulose citrate. Furthermore the binding of SF cellulose citrate, based on untreated cellulose, was also studied.

In the polymer enhanced ultrafiltration method 1000 mg/l Cu(II) concentration was used, and complexation experiments were carried out with carboxymethyl cellulose (CMC, viscosity 25–75 mPs s). The pH of the aqueous solutions was adjusted using 1 M HCl and 1 M NaOH. The filtration measurements were performed with a polyethersulfone ultrafiltration membrane (MOLSEP) having a 10 kDa cut off [19]. Cu concentration in the feed, permeate and retentate solutions were analysed by a photometer (Hach Lange LESA 100) [19].

In the adsorption experiments 50 ml solution of 1 ppm initial concentration of Cu(II) was mixed with polybenzoxazine aerogel (10–80 mg) under constant magnetic stirring. Sodium hydroxide were used for the adjustment of the pH (4-5). The suspensions were filtered after 4–48 h and metal solutions were analysed by using ICP [20].

3. Results

3.1. RP citrate characterization

3.1.1. Effects of initial solution pH on Cu removal

The effect of pH on binding was investigated. As being a weakly acidic cation exchange material, ion binding capacity of RP citrate is greatly depending on the pH of the liquid processed.

When pH was less than 2, the amount of Cu removal was almost undetectable. As pH increased, the amount of Cu removal increased, and the sharpest increase was observed between pH 2 and 3. The maximum value of Cu removal appeared in the range of pH 4 to 5. However, the precipitation of insoluble Cu hydroxide occurred at pH values greater than 5. Therefore pH 4.5 was selected for the subsequent experiments. The pH was adjusted to 4,5 with 10% NaOH solution, using pH meter. The Cu removal as a function of the solution pH is in Fig. 3.

3.2. Influence of contact time on Cu removal

The influence of contact time on Cu removal by RP cellulose citrate is illustrated in Fig 4. The rate of Cu removal was very rapid at the initial stage of sorption, caused by the fast diffusion and sorption of Cu ion onto the external surface of RP citrate. Afterwards the rate of Cu removal declined gradually and reached an equilibrium value. This process was controlled by the pore

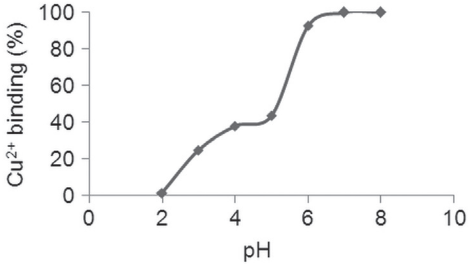

Fig. 3. Cu(II) removal vs. pH (1 h).

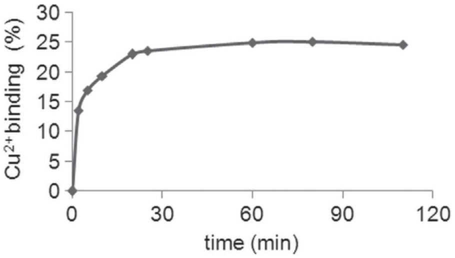

Fig. 4. Cu(II) binding vs. time.

diffusion rate of Cu ions. Thus it was confirmed that the adsorption equilibrium was reached within one hour.

3.2.1. Comparison of effectiveness of various separation techniques

The features of the weak acidic cation exchange material prepared from RP cellulose lignocellulosic feedstock were investigated experimentally. In the binding experiments it was found that 45% of the copper ions were bound. Binding tests were also carried out to determine the non-treated raw-materials ion binding capacity, and it was found it bound only 12% with physical adsorption, which is significant less than in case of RP cellulose. Moreover ion exchange material was prepared from Solka Floc lignin-free pure cellulose and its binding capacity was determined, as well.

In the polymer enhanced ultrafiltration experiments firstly the CMC formed a polymer complex with Cu(II) ions, where the binding sites were the oxygen of ethoxyl groups and the primary alcoholic O atom of glucopyranose rings [4]. This complex exhibits a square planar configuration [21].

In the adsorption measurements it was found that the Cu(II) removal by the polybenzoxazine aerogel was quite efficient: almost 60% of the initial Cu content was removed using 80 mg aerogel [19].

In Fig. 5 our experimental results on ion exchange are compared with data on adsorption and ultrafiltration from literature. It can be seen that highest Cu(II) removal was achieved by the adsorption experiments (60%) using 80 mg aerogel, though the initial conditions were slightly different in the measurements.

In the measurements presented above the pH was adjusted between 4 and 5 [19]. The influence of various pH values was determined in the next serial of ion exchange experiments and the results were compared to the similar measured data obtained in polymer enhanced UF (Fig. 6) [19]. It can be seen that higher pH values have beneficial effect on the Cu(II) removal and around 100% of the ions could be bound/rejected by the methods described (though incidental precipitation of $Cu(OH)_2$ at higher pH might contribute to this behaviour).

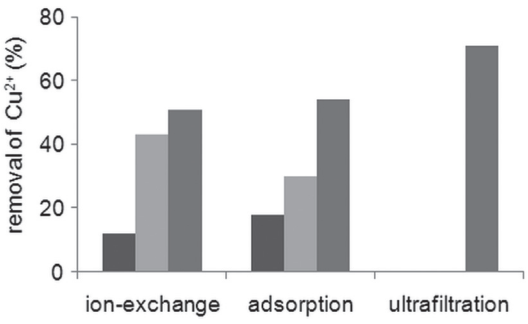

Fig. 5. Comparison of Cu(II) removal by adsorption and ion exchange (ion exchange: ■ non-treated RP cellulose, ■ RP citrate, ■ Solka Floc citrate) (adsorption: ■ 20 mg, ■ 40 mg, ■ 80 mg aerogel added) (■ ultrafiltration).

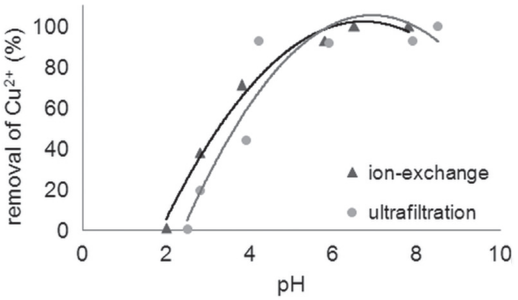

Fig. 6. The effect of pH on the removal of Cu(II) by complexation-ultrafiltration and ion exchange methods.

4. Conclusion

Removal of heavy metal ions from industrial effluents can be carried out by various separation processes. In this work the aims were (i) to manufacture ion exchange particles from lignocellulotic materials formed as a waste in bio-processes; (ii) to apply these particles for heavy metal (e.g., copper ion) removal and (iii) to compare the effectiveness of the process with adsorption and one of the membrane separation techniques: complexation-ultrafiltration method.

To manufacture the ion exchange materials citric acid was reacted with powdered lignocellulosic substance, rapeseed pellet. This material was used in the ion exchange experiments to remove copper ions from aqueous effluents. The experimental results were compared with literature data on Cu(II) removal by a complexation ultrafiltration membrane process and an adsorption method. It was found that complexation-UF is the most efficient technique for the particular task, however the cellulose based ion exchange technique is still a promising alternative for heavy metal removal, considering its capacity, biodegradability and cost-effectiveness.

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