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BIOSORPTION OF COPPER(II) AND CHROMIUM(VI) BY MODIFIED TEA FUNGUS

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The tea fungus was found to have good adsorption capacities for heavy metal ions. In this work it was treated with HCl or NaOH at 20 °C or 100 °C, with the aim to improve its adsorption ability. The sorption of Cu(II) and Cr(VI) ions from aqueous solutions by raw and treated tea fungus was investigated in the batch mode. The largest quantity of adsorbed Cu(II), of about 55 mg/g, was achieved by tea fungus modified with NaOH at 100°C. For Cr(VI), the largest quantity of adsorbed anions, of about 58 mg/g, was achieved by the adsorbent modified with NaOH at 20 °C. It was shown that acid modification of tea fungus biomass was not effective.

KEY WORDS: biosorption, copper(II), chromium(VI), tea fungus, modification

INTRODUCTION

Heavy metals are very harmful as they can accumulate in living tissues. Hence, the pollution caused by them is one of the most critical environmental issues (1). Effluents from various industries may contain excessive concentrations of copper(II) and chromium(VI). It is known that high concentrations of copper are toxic to humans and other organisms (2) and the effects of acute copper poisoning in humans are very serious, with possible liver damage. Chromium(VI) from the electroplating, tanning, painting and similar industries has been reported to be toxic to animals and humans. It is carcinogenic and its bioaccumulation into flora and fauna creates serious ecological problems (3,4).

There are many different methods for the removal of heavy metals from water and wastewater. The existing chemical methods require a large excess of chemicals, giving voluminous toxic sludges. Also, they are generally expensive. In the recent decade, biosorption methods have received considerable attention of researchers all over the world as an economic and eco-friendly option for removal of heavy metals from water and wastewater. The heavy metal adsorption technology by waste microbial biomass is effective, and can sometimes provide better results than natural zeolites and activated carbon, being comparable to synthetic ion-exchange resins (5). In addition, it uses inexpensive biosorbent materials. The maintaining of living microbial populations requires the stable and controllable environment conditions, which is problematic under highly variable condi-

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ons of wastewaters. However, some types of microbial biomass in non-living form can be good biosorbent materials.

The tea fungal biomass is a by-product or waste material from production of kombucha beverage. The kombucha culture is a symbiotic culture of bacteria (genera *Acetobacter*) and one or more yeasts (*Saccharomyces ludwigii*, *Saccharomyces cerevisiae*, *Saccharomyces bisporus*, *Torulopsis* sp., *Zygosaccharomyces* sp.) in floating cellulose mat. It has been investigated as biosorbent for the removal of different heavy metals from water (6-9). This paper is concerned with the effect of different treatments of tea fungus on its adsorption efficiency for copper(II) and chromium(VI). Such examination was done bearing in mind that pretreatment of some adsorbent could improve its adsorption properties, e.g. adsorption capacity, rate of adsorption, prevention of leaching of some undesired substances from adsorbent during adsorption, etc (9, 10).

EXPERIMENTAL

Tea fungus as biosorbent

The tea fungus used for biosorption experiments was obtained from the Faculty of Technology in Novi Sad (Republic of Serbia). The fungal biomass was washed with an adequate amount of distilled water in order to free it from the media components. The fresh fungal biomass was cut by scissors in pieces of 1 x 2 mm and used in the biosorption experiments or for modification.

Modification of the tea fungus

Modification of the tea fungus was performed with an alkali and an acid. The pretreatments with alkali were done in the following way:

1. An amount of 40 g of washed and cut tea fungus was treated with 200 ml of 1 mol/l NaOH at 100°C for 5 minutes,
2. The weighed amount of 40 g of washed and cut tea fungus was treated with 200 ml of 1 mol/l NaOH at 20°C for 1 hour.

The pretreatments with acid were done in the following way:

1. The weighed amount of 40 g of washed and cut tea fungus was treated with 200 ml of 1 mol/l HCl at 100°C for 5 minutes,
2. The weighed amount of 40 g of washed and cut tea fungus was treated with 200 ml of 1 mol/l HCl at 20°C for 1 hour.

After the treatments with NaOH and HCl the tea fungus was washed with distilled water in order to remove the excessive alkali and the acid and dried at 105°C during 20 hours.

Preparation of metal solutions

The stock solutions of metal salts (0.25 mol/l) were prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$ in distilled water. The initial metal concentrations of about 0.4 mmol/l were obtained by dilution of stock solutions, and a real concentration of metal ions was measured before each biosorption experiment. The pH of the adsorbate solu-

tions was adjusted to desired values with 0.1 mol/l HCl or 0.1 mol/l NaOH. Fresh diluted solutions were used for each experiment. All the chemicals used were of analytical grade.

Biosorption experiments

The biosorption experiments were performed by mixing 0.15; 0.25 or 0.5 g/l of tea fungal biomass in 200 ml of the metal ion solution at the optimal pH values, which are pH 4 for Cu(II) and pH 2 for Cr(VI) (6). Batch experiments were carried out at 25°C in Erlenmeyer flasks on a rotary shaker at 200 rpm. Samples were taken after 1 hour and filtered by using filter paper Watman N°1 to remove the suspended biomass and analyze for the residual Cu(II) and Cr(VI). The concentrations of heavy metal ions before and after biosorption were determined using an atomic absorption spectrophotometer (Varian AA-10).

The sorption capacity of the tea fungal biomass was calculated based on the mass balance:

$$q(\text{mg/g})=(C_0-C)/m \quad [1]$$

where q is the amount of metal uptake per unit mass of biosorbent (mg/g); C_0 and C (mg/l) are the initial and residual concentrations of metal ion, respectively, and m is the dry mass of the biosorbent (g/l).

Each batch experiment was carried out in duplicate and average results are presented.

RESULTS AND DISCUSSION

Removal of Cu(II) by tea fungus treated with NaOH and HCl

Adsorption of copper ions by unmodified and differently modified tea fungus was investigated. Figure 1 shows the amounts of copper(II) uptake by unmodified and alkali modified tea fungus, while Figure 2 presents copper(II) uptake by unmodified and acid modified tea fungus.

A very good adsorption efficiency of copper ions was achieved by both unmodified and modified tea fungus; it was better than Cu(II) adsorption by *Neurospora crassa* (10) and many other microbial biomass materials (11), and similar with the adsorption by *Ulva* biomass (12), agricultural wastes (13), poplar sawdust (14), and so on. When tea fungus was applied in a large dose, then a larger surface area was available for adsorption of copper ions. As a result, a smaller amount of copper ions was adsorbed, and smaller differences between unmodified and modified tea fungus were observed than in the case of the application of a smaller adsorbent dose, i.e. a smaller available adsorbent surface area. The results presented in Figure 1 show that the modification of tea fungus by alkali in any case improved adsorption of copper(II). The tea fungus modified with NaOH at 100°C had significantly higher quantity of adsorbed copper(II) than the unmodified tea fungus or modified with NaOH at 20°C. Obviously, the modification at higher temperature was better, but it is energy consuming, too.

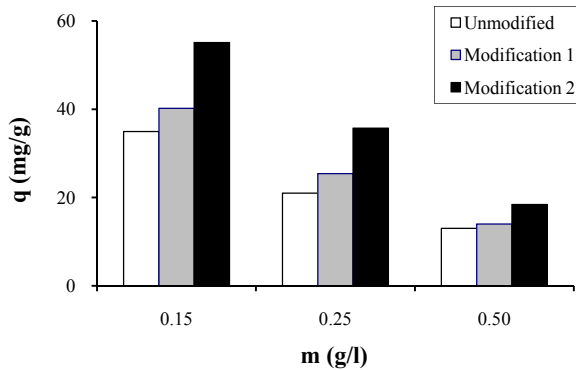


Figure 1. Removal of Cu(II) by unmodified tea fungus and tea fungus treated with 1 mol/l NaOH at 20°C for 60 minutes (Modification 1) and with 1 mol/l NaOH at 100°C for 5 minutes (Modification 2)

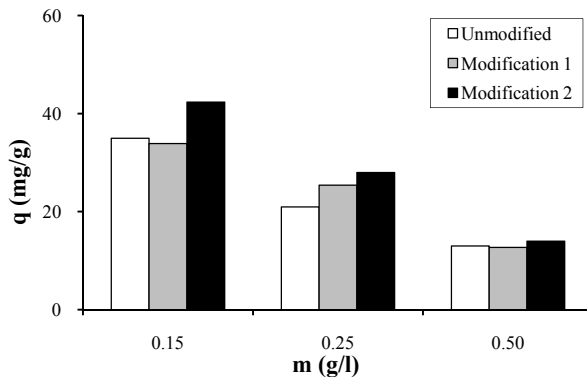


Figure 2. Removal of Cu(II) by unmodified tea fungus and tea fungus treated with 1 mol/l HCl at 20°C for 60 minutes (Modification 1) and with 1 mol/l HCl at 100°C for 5 minutes (Modification 2)

The modification of tea fungus by acid gave worse results compared to the adsorption by adsorbent modified with alkali. Similar results were obtained when different agricultural adsorbents were modified by acid and alkali solutions (13). Khosravi et al. (15) found that NaOH increased, while HCl decreased the adsorption capacity of *Azolla filiculoides* for Pb(II), Cd(II), Ni(II) and Zn(II). On the other hand, it was found that acid modification of poplar sawdust did not improve adsorption of copper(II), but enhanced zinc(II) adsorption by about four times (16).

It is well known that the solution pH can significantly influence adsorption of heavy metal ions. In contrast to the slight increase of the pH after the adsorption on unmodified poplar sawdust (16), and on the alkali modified one (14), it was observed that the pH of the solution after adsorption of copper ions by acid modified poplar sawdust was accompanied by a slight decrease. Probably, that was the reason of lower adsorption ability of

acid modified tea fungus. However, acid modification at 100°C slightly improved Cu(II) adsorption, but less than the modification with alkali. After all, it can be said that the high temperature affects the adsorption characteristics of tea fungus by changing its structure and/or surface conditions.

Removal of Cr(VI) by tea fungus treated with NaOH and HCl

The Cr(VI) ions (from $K_2Cr_2O_7$) in the solution of the pH 2 are predominantly in the form of $Cr_2O_7^{2-}$ anions (17). The adsorption of these anions is completely different compared to the adsorption of Cu^{2+} . The chromium(VI) adsorption by unmodified and alkali modified tea fungus is presented in Figure 3, and its adsorption by unmodified and acid modified tea fungus in Figure 4.

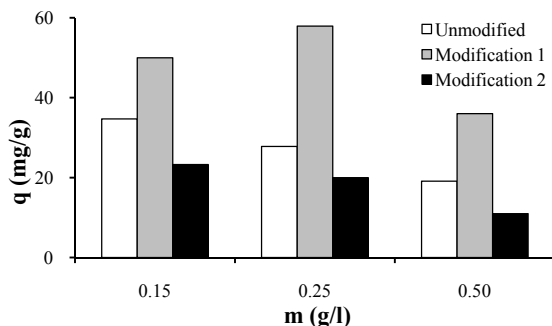


Figure 3. Removal of Cr(VI) by unmodified tea fungus and tea fungus treated with 1 mol/l NaOH at 20°C for 60 minutes (Modification 1) and with 1 mol/l NaOH at 100°C for 5 minutes (Modification 2)

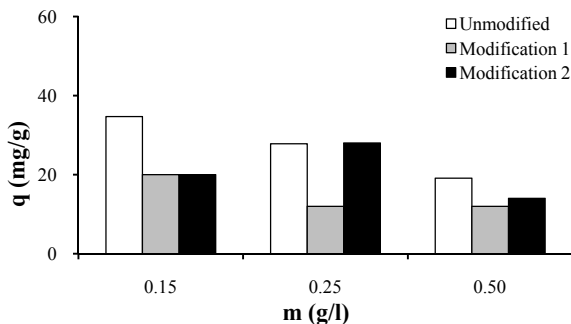


Figure 4. Removal of Cr(VI) by unmodified tea fungus and tea fungus treated with 1 mol/l HCl at 20°C for 60 minutes (Modification 1) and with 1 mol/l HCl at 100°C for 5 minutes (Modification 2)

The adsorption of dichromate anions by both unmodified and modified tea fungus was better than their adsorption by many other microbial biomass materials (11). Alkali modification at 20°C led to the significantly improved adsorption of dichromate anions, but the modification at 100°C suppressed the adsorption. Alkali modification at high temperature led to unwanted changes in the adsorbent, which decreased the chromium(VI)

adsorption. Mild modification had a beneficial effect that was manifested even when the large surface of the adsorbent was available (when the large quantity of adsorbent was used).

Although the adsorption of dichromate anions was better at lower pH values, acid modification of tea fungus did not contribute to a better adsorption. Contrary, the amount of adsorbed anions was lower than in the case when the unmodified tea fungus was used.

CONCLUSIONS

This paper deals with the adsorption of copper(II) and chromium(VI) ions by unmodified and modified tea fungus biomass – a waste product from kombucha production. The modification was done by 1 mol/l NaOH or 1 mol/l HCl at 100°C for 5 minutes, or at 20°C for 1 hour. When the tea fungus was applied in a larger dose, then the larger surface area was available for adsorption, and consequently, a smaller amount of ions was adsorbed per mass unit of the adsorbent. In that cases there was not strong competition for active sites on the adsorbent surface and, because of that, the lower differences between unmodified and modified adsorbents were observed. It was shown that both unmodified and modified tea fungus had significant adsorption capacity, similar to some other biosorbents. Modification with NaOH gave better results. The largest quantity of adsorbed copper(II), of about 55 mg/g, was achieved using tea fungus modified with NaOH at 100°C. For chromium(VI), the largest quantity of adsorbed anions, of about 58 mg/g, was achieved by the adsorbent modified with NaOH at 20°C. It was shown that acid modification of tea fungus biomass could not be recommended.

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БИОСОРПЦИЈА Cr(VI) И Cu(II) МОДИФИКОВАНОМ ЧАЈНОМ ГЉИВОМ

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Познато је да су тешки метали штетни по здравље људи и да се могу акумулирати у живим ткивима. Стога, загађење животног окружења изазвано тешким металима представља једно од најбитнијих питања заштите животне средине. Ефлуенти који потичу из различитих индустрија могу садржавати повећане концентрације јона бакра(II) и хрома(VI). Бакар у повећаним концентрацијама је токсичан за људе и друге организме, а ефекти акутног тровања баком код људи су веома озбиљни,

са потенцијалним оштећењем јетре код продужене изложености. За хром(VI) је такође утврђено да је токсичан за животиње и људе, канцероген и да се акумулира у флори и фауни доводећи до еколошких проблема.

У ранијим истраживањима, потврђено је да чајна гљива поседује добар адсорпциони капацитет за јоне тешких метала. У овом раду чајна гљива је третирана хлороводоничном киселином и натријум-хидроксидом на 20°C и 100°C, са циљем да се побољша њена адсорпциона способност. Адсорпција Cu(II) и Cr(VI) јона из воденог раствора сировом и третираном чајном гљивом је испитивана у шаржним условима. Највећа количина бакар(II) јона, око 55 mg/g, је адсорбована чајном гљивом модификованом натријум-хидроксидом на 100°C. У случају хрома(VI), највећа количина ових јона, око 58 mg/g, је адсорбована чајном гљивом модификованом натријум-хидроксидом на 20°C. Такође, утврђено је да кисела модификација негативно утиче на адсорпциону способност чајне гљиве за адсорпцију Cu(II) и Cr(VI) јона.

Кључне речи: биосорпција, хром(VI), бакар(II), чајна гљива, модификација

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