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USE OF RICE HULLS AND BRAN FOR REMOVAL OF METAL IONS FROM WASTEWATER

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Rice hulls and bran from three cultivars (Monticheli, P-76/6 and Prima Risaka) were evaluated as adsorbents for removal of metal ions from aqueous solutions. All of them showed an adsorption potential which is different for particular metal ions. The hulls and bran pretreated with 5 % NaOH showed an excellent adsorption capacity for removal of Co(II) and Cr(III). The hulls and bran of Monticheli and bran of Prima Riska are the best adsorbent for removing Co. They removed 100% Co from the aqueous solution of concentration 200 mg/l. About 91 % of Cr was adsorbed by hulls of Prima Riska, hulls and bran of P-76/6 and bran of Monticheli. The hulls and bran of all three cultivars are less effective adsorbents for removal Cu(II) and Ni(II). The bran and hulls of Monticheli removed the highest percent of Cu, 80.5 % and 45.6 % respectively. The hulls and bran of the three rice cultivars showed the least capacity of adsorption of Ni. The bran of P-76/6 adsorbed about 50 % of Ni, while the byproducts of two other cultivars only 37.5%.

ПРИМЕНА НА ОРИЗОВИТЕ ЛУШПИ И ТРИЦИ ЗА ОТСТРАНУВАЊЕ НА МЕТАЛНИ ЈОНИ ОД ОТПАДНИ ВОДИ

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Оценувана е способноста на оризовите лушпи и трици од три сорти ориз (монтичели, Р-76/6 и прима риска) за атсорбирање на метални јони од водни раствори. Сите покажаа атсорпционен потенцијал кој се разликува кај одделни испитувани метални јони. Лушпите и триците претходно обработени со 5% NaOH покажаа одличен капацитет на атсорпција на Co(II) и Cr(III). Лушпите и триците од сортата монтичели и триците од прима риска се најдобри атсорбенти на Co. Тие го извлекуваат 100% Co од воден раствор со концентрација од 200 mg/l. Околу 91% од Cr е адсорбиран од лушпите на прима риска, лушпите и триците на Р-76/6 и триците на монтичели. Лушпите и трициите на сите три сорти се помалку ефикасни атсорбенти за отстранување на Cu(II) и Ni(II). Трициите и лушпите од монтичели отстрануваат најголем процент на Cu, 80,5% и 45,6% соодветно. Лушпите и трициите од трите сорти ориз покажаа најмал капацитет за атсорпција на Ni. Трициите од Р-76/6 атсотрбираа околу 50% од Ni, додека споредните продукти на другите две сорти ориз само 37,5%.

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Introduction

During recent years considerable attention has been given to the use of agricultural residues in the removal of havy metal ions from aqueous solutions, especially in wastewater treatment in textile and agricultural industry [1]. Some research has shown that commodity crop residues, such as peanut hulls and skins [2], bagasse pith [3] and rice milling byproduct (hulls and bran) [4] have varying degrees of affinity for metal ions in aqueous solution. Therefore industrial application would increase the value of this byproduct. Republic of Macedonia annually has produced over 18000 t of rough rice [5]. Process of rough rice milling includes several main steps: clearing of extraneous matters, hulling, polishing and grading. Hulled rice is commonly called brown (cargo) rice. After hulling the germ and outer bran are removed in resultant bran meal, and thus obtained mixture of whole and broken rice is separated and prepared to be sold. The percentage of byproducts (hulls and bran) depends on milling rate, type of rice and other factors. An approximate proportions of the products of the milling are: hulls 20%, bran 10%, broken rice 1-17% and polished rice 50 - 65%. It means that about 3600 t of hulls and over 1800 t of bran are appeared as byproducts per a year in Macedonia. Our aim was to evaluate capacity of the hulls and bran from three rice cultivars for adsorption of metals commonly found in industrial wastewater.

Experimental

Rice hulls and bran were obtained from three cultivars, Monticheli, Prima riska nd P-76/6 cultivated on the experimental filed of Kochani, Macedonia. They were prepared by soaking in 5% NaOH or 5% HCl for 2 hr, washed to remove NaOH/HCl and dried. The bran was composed of fine particles, while hulls were additionally milled in coffee grinder. Adsorption of metal ions were run at metal concentrations of 200 mg/dm^3. Suspensions of 0,5 g of hulls or bran and 50 ml solutions of CoCl 6H$_2$O, CrCl$_2$(H$_2$O)$_4$Cl2H$_2$O, CuSO$_4$ 5H$_2$O and NiSO$_4$+7H$_2$O in polyethylene bottles were stirred for 2 hr at 80 rpm with Teflon coated magnetic stirrer. Than it was centrifugated for 15 min at 3000 rpm and the supernatants were filtered through glass filters to remove any suspended particles. Concentrations of metal ions in the solutions were determined from the concentration curves obtained at corresponding wave lenth on PYE UNICUM 400 spectrophotometer.

Results and Discussion

Particle size distribution

Particle size distribution of hulls and bran of the three investigated cultivars is presented on Fig.1. The most part (79-87%) of the particles of the hulls were with dimensions of 1-0,5 mm, about 11-17% varied between 0,5 and 0,25 mm and only 2-7% were smaller than 0,25 mm, Fig.1a. However, about 50 – 60% of the particles of the brans were with dimensions between 1-0,5 mm, 20 – 30% with dimensions of 0,5-0,25 mm and 10-30% were smaller than 0,25 mm, Fig.1b. This results indicated that hulls and bran used as adsorbents for removing metal ions from aqueous solutions were with different active surfaces. At advance it was expected these differences to have an influence on adsorption capacity.
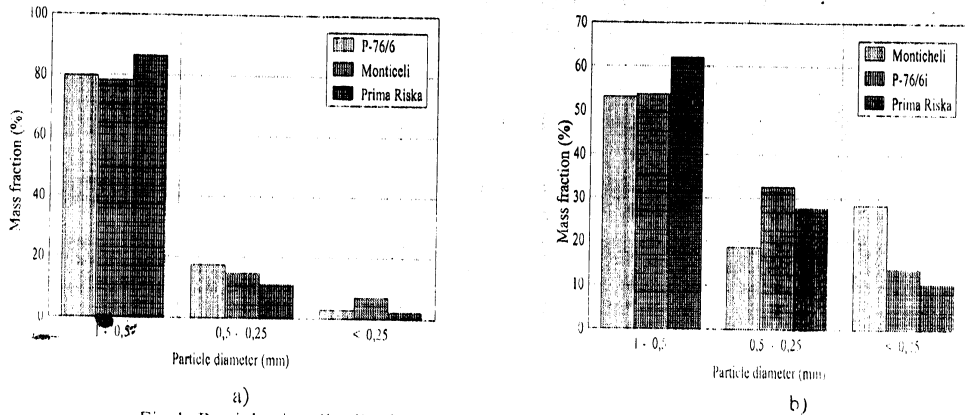
Fig.1. Particle size distribution of a) hulls and b) bran of three rice cultivars

Adsorption capacity of hulls and bran

Adsorption of different matal ions from aqueous solutions by hulls and bran of the three investigated rice cultivars: Prima Riska, Monticheli and P-76/6 , pretreated with 5% NaOH is shown on Fig.2.
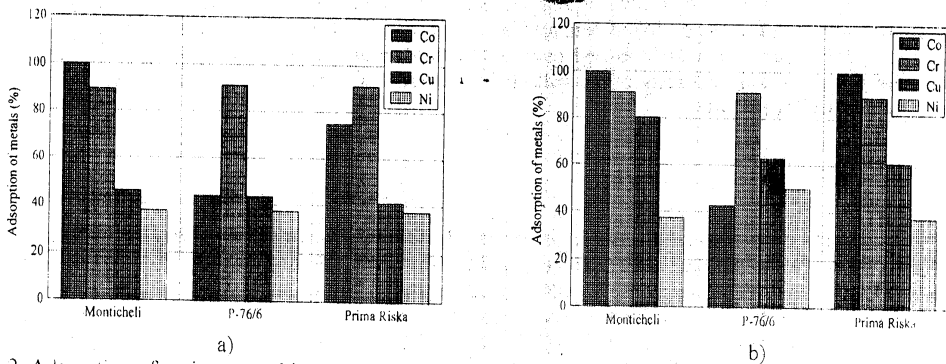

Fig.2. Adsorption of various metal ions (200 mg/L) to a) hulls and b) bran, of three rice cultivars treated with 5% NaOH

The hulls and bran of the all three investigated rice cultivars have shown adsorption capacity for metal ions from aqueous solutions, however it differs for particular metals. The hulls and bran of Monticheli and bran of Prima riska are the best adsorbent for removing Co. They adsorbed 100% Co from its aqueous solution with concentration of 200 mg/L . Adsorption of about 91% Cr was attained equally by hulls of Prima Riska, hulls and bran of P- 76/6 and bran of Monticheli. The bran and hulls of Monticheli removed the highest percent of Cu, 80,5% and 45,6 % respectively. The hulls and bran of the three rice cultivars have shown the least capacity of adsorption of Ni. The bran of P-76/6 adsorbed about 50% of Ni, while the byproducts of two other cultivars only 37,5%. Marshall et al. [4] removed 20,1% of total Co (II), 12,6% of Cr (III), 26,9% of Cu (II) and 22% of Ni (II) when used aqueous solutions with 100 mg/L of metal ions and similar treated hulls. The adsorption capacity of hulls and bran depends of the content of polimeric components like protein and hemicellulose. They attract metal ions with theirs negatively charged groups. However, if the part of the charges are occupied with endogenously present metals the adsorption capacity for particular metal ions would be lower. The right answer about different adsorption capacity among the three cultivars for the investigated metal ions could be obtaied if compositional analyses of the hulls and bran is made.

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