University of Belgrade
Technical Faculty in Bor

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and Industry of Serbia

XV International Mineral Processing & Recycling Conference

IMPRC
INTERNATIONAL MINERAL PROCESSING & RECYCLING CONFERENCE

Proceedings

Editors:
Jovica Sokolović
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17-19 May 2023 | Belgrade SERBIA

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REMOVAL OF HEAVY METAL IONS FROM MULTIMETALLIC SOLUTION BY MODIFIED OAT STRAW

J. Dimitrijević[1#], S. Jevtić[2], A. Marinković[2], M. Simić[1], M. Koprivica[1], J. Petrović[1]
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ABSTRACT – In this paper, the ability of waste biomass as an adsorbent was investigated. Oat straw was chosen as the starting raw material. In order to improve the adsorption capacity this material was modified with selected deep eutectic solvent (DES). Changes in the structure of the native and modified samples were examined using the SEM analysis. The efficiency of the adsorption of heavy metal ions from a multimetal solution was tested on the modified oat straw. The maximum obtained capacities of lead, copper and zinc ions were 77mg/g, 29.5mg/g and 44.1mg/g, respectively. The obtained results showed that adsorption follows pseudo-second-order kinetics model that imply chemisorption as a rate controlling step.

Keywords: Adsorption, Oat Straw, DES Solution, Biomass Modification.

INTRODUCTION

The rapid technical and technological development in recent years has led to greater use of natural waters and their contamination. Various branches of industry such as pharmaceuticals, mining, mineral processing, production of artificial fertilizers and construction materials, oil refining and ferrous metallurgy are among the main polluters of the environment [1]. On that occasion, heavy metals, organic components, dyes, pesticides, drugs, which have a harmful effect on the environment, enter the waterways. Due to their toxicological and chemical properties, heavy metals represent a major problem for the preservation of the environment. They are toxic, non-degradable in water and soil, subject to bioaccumulation, which leads to reaching the food chain. Heavy metals in smaller quantities are necessary for the normal functioning of the organism, while to a greater extent they cause serious damage or can have a lethal effect. Accordingly, more and more attention is being directed to research related to the preservation of the environment in order to reduce or completely prevent the pollution by heavy metals [1-3].

Different traditional methods such as: sedimentation, oxidation-reduction, ion exchange, coagulation and flotation, membrane filtration and others have been greatly used for the removal of pollutants from waste water [3,4]. Traditional technologies also have disadvantages such as economic profitability due to high operating costs, insufficient selectivity, producing large amount of waste sludge, the increasing

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attention of the scientific public is focused–in finding more adequate and accessible solutions [4,5].

An increasing number of researches are directed towards the development of alternative remedies for the removal of semi-titanium from water. One of the increasingly applicable alternative methods is biosorption. Biosorption is a technique characterized by high efficiency, accessibility, economic profitability, selectivity and ecological acceptability for the removal of heavy metals from wastewater [1,4,5]. Easily available, cheap, waste natural materials are used, due to their physical and chemical characteristics; they bind pollutants to the surface. In order to increase the additional adsorptive properties, different methods of biomass modification are used to increase the binding surface and the number of active binding sites. Various alkaline and acid modifications are widely used. Recently, there has been an increasing use of environmentally acceptable deep eutectic solvents (DES) as innovative green liquid for the treatment of lignocellulosic biomass, in order to obtain the desired characteristics for potential further application [6,7]. DES solvents consist of hydrogen bond donors and acceptors, which affect biomass degradation, that is, partial or complete degradation of lignin from biomass. The biomass after the interaction with the DES gives a more porous structure in comparison with the native sample [8].

Oat straw is a readily available, inexpensive bio-waste generated after harvesting of oats. Due to the large production of straw after the harvest, are more and more attention is being directed to its further application. Precisely for this reason, in this paper, the modification of oat straw with DES solvent as an adsorbent for liquid metals from water resources was examined. In order to examine the influence of the modification on the sorbent SEM analysis was performed. The paper presents the results obtained after the application of modified oat straw for the removal of lead, copper and zinc from a multi-metallic solution.

EXPERIMENTAL

The oat straw used in this research was obtained after the oat harvest in Banat (a region in Serbia). The straw was collected directly from the field, washed a couple of times to avoid impurities and dried at room temperature. The dried oat straw was ground, sieved and dried to a constant mass at 105°C.

In order to degrade lignocellulose in oat straw, DES solvent was used. The DES solvent is prepared by mixing the ionic liquid choline arginate (IL) and a sufficient amount of urea. The reaction was carried out in a reflux condenser with constant stirring at 40°C [9]. Obtained modified oat straw was dried in a dryer to constant mass and used for further adsorption experiments.

The $Pb(NO_3)_2x6H_2O$, $Cu(NO_3)_2x3H_2O$ and $ZnSO_4x7H_2O$ were used for the preparation of the working solution. All used chemicals were of analytical grade.

Morphological characteristics of the sample before and after modification were investigated by scanning electron microscopy (SEM) using Jeol JSM-6610LV, at 20 keV. Before recording, the samples were dried at 105°C, impregnated with gold and placed on a carbon.

Adsorption experiments were performed in a batch system. The experiment was carried out at room temperature and pH value 5. The influence of contact time was tested in different time intervals from 15 to 1440 min. About 0.04 g of modified oat straw and 40 ml of multi-metal solution were added to 100 ml Erlenmeyer flasks. The initial concentrations of lead, zinc and copper were 1mM, 1,5mM and 1.5 mM, respectively. The suspensions were stir on an orbital shaker mixed at room temperature at 250 rpm and filtered. At the end of the adsorption experiment, the metal concentration in the filtrates was measured by the ASS method on a Perkin Elmer 900T.

RESULTS AND DISCUSSION

The morphological characteristics of the material before and after modification were examined with a scanning electron microscope (SEM). Figure 1 shows the results of the analysis. According to the SEM micrograph, it was observed that there was a change in the appearance of the surface of the modified sample. Changes on the surface are caused by degradation of lignocellulose after modification with DES. An increase in the number of channels, voids and pores is observed compared to the relatively smoother appearance of native oat straw. In oat straw, a smaller number of cavities and channels are observed [1,10,11]. Figure 1b, which represents the modified sample, shows numerous cavity channels and a more heterogeneous structure compared to the native sample. The results obtained in this way support the fact that the use of degradability of DES leads to the degradation of lignocellulose. [10] A surface with more pores and channels is more suitable for adsorption due to the easier possibility of ion diffusion, as well as more sites for metal binding.

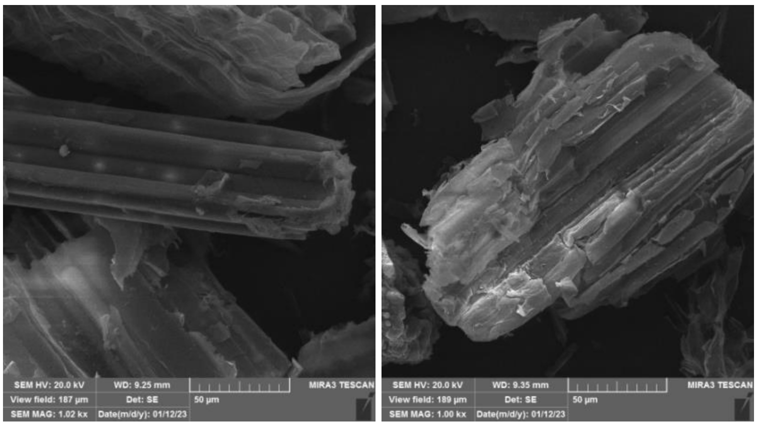

Figure 1 SEM images of oat straw before and after modification with DES

Preliminary adsorption tests revealed that the modified oat straw has a higher affinity for metal ion binding than the native one. Accordingly, the influence of time was examined only on the modified material. The influence of contact time on the adsorption of each metal is shown separately in the Figure 2. The results indicate that with increasing time, the efficiency of removing metal ions from the aqueous solution also increases. After 4 hours, there were no significant changes in the capacity. The maximum capacities for lead, zinc and copper are 77mg/g, 29.5mg/g and 44.1mg/g respectively. The obtained results indicate that the binding sites on the surface of the adsorbent are filled due to high competition between the site ions in the solution [12]. Similar results were obtained by Cherono et al. [13], which also has a slight trend of decreasing capacity for certain metals after 24 h, which is noticeable here for zinc. The multiple efficiency of metal ion removal was faster on the beginning, which is attributed to the larger number of active sites that become filled over time. Adsorption efficiency is highest for lead ions.

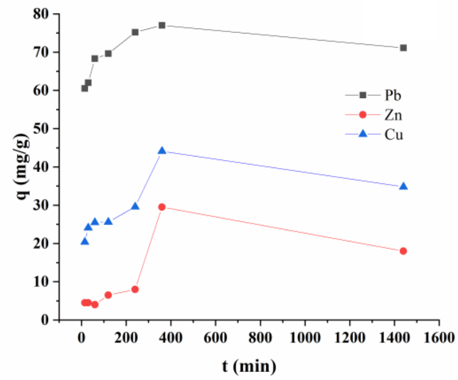

Figure 2 The effect of time during the adsorption of lead, copper and zinc ions using modified oat straw

Figure 3 shows graphs representing the pseudo first and pseudo second kinetic models for the adsorption of lead, copper and zinc metals from a multimetal solution after adsorption of modified oat straw. Based on the obtained results, it can be concluded that the adsorption kinetic for all metals follows pseudo second-order kinetic model. This is supported by the data presented in Table 1. Obtained values (Table 1) suggesting that chemisorption was an important mechanism responsible for the binding of investigated metal ions to the modified oat straw surface [14]. The results obtained during this study support the fact that the modification process with DES was successful.

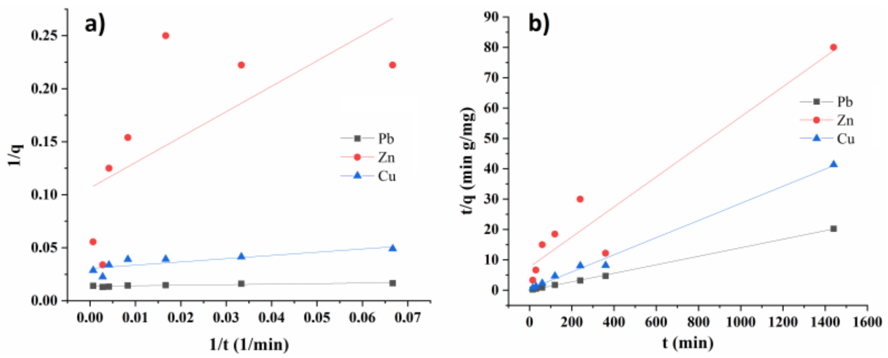

Figure 3 Curves of kinetic adsorption of metals on modified oat straw a) pseudo first models b) pseudo second models

Table 1 Kinetic parameters

Modified oat straw	Pb	Zn	Cu
$q_{eq, exp}$ [mg/g]	77.00	29.5	44.1
Pseudo-First-Order Model			
$q_{eq,cal}$ [mg/g]	73.42	9.40	32.77
k_1 [1/min]	3.69	22.53	9.99
R^2	0.8055	0.4517	0.6992
Pseudo-Second-Order Model			
$q_{eq,cal}$ [mg/g]	71.38	20.21	35.43
κ_2 [g/mg min^{-1}]	0.2914	0.0065	0.0007
R^2	0.9994	0.9129	0.9939

CONCLUSION

In this work, the possibility of using modified oat straw as a biosorbent for the removal of heavy metals from waste water was investigated. In order to improve the adsorption capacity of oat straw, it was modified with DES solvent. In order to compare the structural characteristics of the material before and after modification, characterization was performed using SEM analysis. Based on the obtained results, it was observed that there are changes in the structure, i.e. degradation of lignocellulose. Adsorption experiments performed on modified oat straw showed that adsorption follows pseudo-second-order kinetics and approaches chemisorption as binding mechanism. Results from this study indicate that competition between ions from multimetal solution for binding sites on adsorbent surface occurs. Besides, under these conditions, the best ability of lead removal was achieved.

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