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# Modification of rice hull and sawdust sorptive characteristics for remove heavy metals from synthetic solutions and wastewater

Fatemeh Asadi *, Hossien Shariatmadari [1], Noorallah Mirghaffari [2]

*Soil and Water Research Institute, P.O. Box 14155-6185, Tehran, Islamic Republic of Iran*

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**Abstract**

In this work two modified agricultural residues, rice hull and sawdust were examined as sorbents to remove heavy metals Pb(II), Cd(II), Zn(II), Cu(II) and Ni(II) from synthetic solutions or wastewater samples. To modify their sorptive characteristics, samples were treated with HCl, NaOH and heat. The sorption of the heavy metals from the synthetic solutions was increased with pH and initial concentration. In pH 5, Pb(II) and Cd(II) showed the highest sorption and Cu(II), Zn(II) and Ni(II) showed the following orders, respectively. Sorption capacity of rice hull was higher than sawdust. The modifications changed the sorption capacity of the natural sorbents in the following order base > heat > natural > acid. The sorption isotherms of sorbents were best described by the Freundlich and Langmuir models. The basic treated rice hull and sawdust followed by the heat treated rice hull sorbed the maximum of heavy metals from the industrial wastewater samples. In the column experiment, the synthetic solutions and the wastewater samples gave almost the same results as the suspensions. The recovery of the columns using water and HCl showed positive results. Commercial sorbents removed Pb(II), Zn(II) and Ni(II) a little more than rice hull.


*Keywords:* Sawdust; Rice hull; Wastewater; Sorptive characteristics; Column experiment

## 1. Introduction

Iran is located in arid–semiarid regions of the world with very limited water sources. Many human activities such as mining, metallurgy and industrial wastewater implications cause heavy metal contamination of surface and ground water and increase the risk of water crises in the country. These metals have large significance effects on the economic and public-health of ecosystems [1]. On the other hand, properly treated wastewater may be applied as water for irrigation or it may be discharged to ground water sources, which in both cases, it lowers the water shortage. The removal of metal ions from effluents is important to many countries of the world both environmentally and for water re-use. Agricultural residues are usually available at low cost. Wood- and agricultural-based fiber can be produced from these residues and used as filters to remove various types of contaminants from water. There are many studies on the features and advantages of the unconventional removal method of heavy metals such as biosorption and use of low cost agricultural by-products. The biosorption (sorption of metallic ions from solutions by live or dried biomass) offers an alternative to the remediation of industrial effluents as well as the recovery of metals contained in other media. Biosorbents are prepared from naturally abundant and/or waste biomass [1]. In recent many reports using low cost agricultural by-products, such as peanut and hazelnut shells, pine bark, rice straw, rice hull, rice bran, soybean and cotton seed hulls, wool, sawdust, etc., instead of ion-exchange resins have been documented [2–10]. These materials have naturally adsorption capacities for heavy metals. However, this capacity is low as compared to commercially ion-exchange resins, but different modifications, e.g. base, acid, heat and dyestuff treatments have shown great promise in improving the cation-exchange capacity of agricultural by-products. They produced a higher value product with potentially lower costs as compared to commercially available ion-exchange resins.

* Corresponding author at: Soil and Water Research Institute, No. 3, North Kargar Avenue, Tehran, Islamic Republic of Iran.
Tel.: +98 21 88021089/9125377960; fax: +98 21 88634006.
*E-mail address:* nel1355@hotmail.com (F. Asadi).
[1] Department of Soil Science, Faculty of Agriculture, Isfahan University of Technology, Isfahan, Islamic Republic of Iran.
[2] Department of Environmental Science, Faculty of Natural Resources, Isfahan University of Technology, Isfahan, Islamic Republic of Iran.

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Verma et al. [11] reported that there are several components, namely protein, lignin, cellulose and hemicellulose in rice hull. These components have the potential to adsorb metals. The lignocellulose (lignin, hemicellulose and cellulose together) consists 74.1% in rice hull; however, this fraction undoubtedly contributes substantially to metal ion adsorption for these by-products. Functional groups within the skeletal structure and surface of the cell wall coordinate and complex the metal ions [12]. Laszlo and Dintzis [13] showed that lignocellulose has ion-exchange capacity and general sorptive characteristics, which are derived from their constituent polymers and structure. The polymers include extractives, cellulose, hemicelluloses, pectin, lignin and protein. These are adsorbents for a wide range of solutes, particularly divalent metal cations. Lignocellulosic resources all contain, as a common property, polyphenolic compounds, such as tannin and lignin, which are believed to be the active sites for attachment of heavy metal cations [14–16]. Lee and Rowell [17] showed that lignocellulosic fibers with the highest level of heavy metal removal such as kenaf bast had a very low level of lignin, showing that removal of heavy metals does not high correlate with lignin content. Cotton, with about 1% lignin, was very low in metal ion sorption. All of the fibers containing lignin remove heavy metal ions therefore lignin does play a role in metal ion sorption. Cell wall chemistry and architecture may also be important factors in the sorption of heavy metals from aqueous solutions using lignocellulosic fiber. Basso et al. [18] found a direct correlation between heavy metal sorption and lignin content of lignocellulosic materials. Also they noted that the cell wall structures and compositions were different for the different lignocellulosics selected, which may have also influenced heavy metal sorption. Lignocellulosic materials are very porous and have a very high free surface volume that allows accessibility of aqueous solutions to the cell wall components. One cubic inch of a lignocellulosic material, for example, with a specific gravity of 0.4, has a surface area of 15 $ft^2$. Even when the lignocellulosic material is ground, the adsorptive surface increases only slightly. Lignocellulosic materials are hygroscopic and have an affinity for water. Water is able to permeate the non-crystalline portion of cellulose and all hemicellulose and lignin materials. Acemioglu and Alma [19] postulate that metal ions compete with hydrogen ions for the active sorption sites on the lignin molecules. They also conclude that metal sorption onto lignin is dependent on both sorption time and metal concentration.

Sawdust is one of the cheapest and abundantly available adsorbent that has the capacity to adsorb and accumulate heavy metals from waters and wastewater. Metal ions connect to functional groups of sawdust such as COOH and OH and release $H^+$ ions. Main mechanisms of ion connection to cellulosic sorbents are chelation, ion-exchange, complexing with functional groups and making hydrogenic bounds [20]. Researches have shown that heavy metals such as Cu(II) in reaction with cellulosic materials as sawdust accumulate in secondary septum of wood. This septum is poor from lignin and affluent on cellulose [7]. Basso et al. [18] have used sawdust to remove Cd(II) and Ni(II) from aqueous solution. Sciban and Klasnja [21] have studied the abilities of different types of wood sawdust and wood originate materials (Sawdust of poplar, willow, fir, oak and black locust wood, pulp and Kraft lignin) for removing some toxic heavy metal ions from water.

Modification processes of agricultural by-product increase adsorption capacity. Active carbon made of rice hull with high specific surface area and sorption capability of amorph $SiO_2$ is a biological filter in water and wastewater purification. Active carbon of rice hull able to remove of heavy metals as Cd(II) and Pb(II) [22]. Surplus, low value agricultural by-products can be made into granular activated carbons (GACs) which are used in environmental remediation. Oxidized GACs made from soft lignocellulosics such as soybean hull, sugarcane bagasse, peanut shell, and rice straw adsorbed from a mixture higher amounts of $Pb^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ than any commercial GACs. Commercial GACs adsorbed only $Pb^{2+}$, $Cu^{2+}$ and $Cd^{2+}$ [23]. Treatment of biosorbents with NaOH solution positively affected adsorption capacity of Pb(II) and Cu(II) [4]. One percent sodium hydroxide can extract major amounts of the hemicelluloses and part of the lignin along with a major portion of the extractives. Carbohydrates, such as parts of the hemicelluloses, starch and pectic material, proteins, alkaloids, inorganic materials, such as $Ca^{2+}$, $K^+$, $Mg^{2+}$, $Na^+$ and $Fe^{2+}$, some phenolic substances, oxalate, citrates, humic acid-like substances, mucilage, gums, and uronic acids are extractable by hot water. Extracting lignocellulosic fibers with different solvents will also change the accessibility of heavy metal solutions to cell wall components. Rice hulls, when coated with the reactive dye of Procion Red or Procion Yellow, was found to be highly effective for removal of many metal ions from aqueous solutions both in batch and column method [24]. The potential of cheap cellulose-containing natural materials such as coir, jute, sawdust and groundnut shells for removal of Pb(II) from aqueous solution of lead nitrate increased after modifying them with a monochlorotriazine type of dye. This was attributed to chelation and an ion-exchange mechanism [20].

Our objectives in this work were to study the modification of sorptive properties of rice hull and sawdust in order to increase the power of heavy metal removal from aqueous solutions and wastewater and study the removal efficiency of heavy metals by low cost sorbents comparing with commercial active carbon and resin.

## 2. Material and methods

### 2.1. Sorbent materials

Dried samples of rice hull (*Lenjan*) and sawdust (*Papullus*, sp.) were milled and then passed through 1 mm sieve. Some characteristics of sorbents such as CEC,[3] elemental composition (percentage of C, O, Al, Si and Ca) and surface area were determined by ammonium acetate, SEM[4]-EDX (Philips model xL 30 series) and $N_2$-BET[5] methods, respectively, before and

[3] Cation-exchange Capacity.
[4] Scanning Electron Microscopy.
[5] Brunauer–Emmett–Teller.