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

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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.

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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.

Table 1
Some chemical and physical characteristics of sawdust and rice hull before and after treatments

Treatment	%C	%O	%Al	%Si	%Ca	CEC ($cmol_c\ kg^{-1}$)	Specific surface area ($m^2\ g^{-1}$)
Sawdust							
Raw	26.3	71.4	0.3	0.5	1.5	68.8	0.5
Acid	27.3	69.9	0.1	0.7	0	35.7	0.8
Base	25.6	72.3	0.2	0.5	1.4	94.3	0.3
Heat	23.9	63.8	0.1	0.4	1.5	112.4	7.5
Rice hull							
Raw	3.2	53.2	0.9	38.9	0.1	54.4	0.7
Acid	3.3	58.9	0.5	33.6	0	44.6	4.1
Base	2.4	74.3	0.2	21.1	0.1	70.8	4.3
Heat	2	52.5	0.9	43.6	3	126.8	73

Table 2
pH and heavy metals concentration ($mg\,l^{-1}$) in wastewater samples

Wastewater	pH	Pb(II)	Cd(II)	Zn(II)	Cu(II)	Ni(II)	Fe(II)
Shahin-shahr	8.27	0.28	–	0.44	0.26	2.42	–
Zoebahan	8.30	0.07	–	0.04	0.04	0.04	0.10
Plating (1)	13.9	1.79	0.72	1152	9.94	1.13	–
Plating (2)	12.5	1.00	1.00	1114	15	3.02	3000

after modification treatments (Table 1). FTIR[6] spectroscopy was used to monitor the course and extent of the sorption reactions.

2.2. Synthetic solutions

The stock solutions ($1000\,mg\,l^{-1}$) were prepared in distilled water using zinc, copper, nickel, cadmium chloride and lead nitrate (Merck). All working solutions were prepared by diluting the stock solution with distilled water. HCl and NaOH were used for changing of solution pH.

2.3. Wastewater samples

Four wastewater samples were obtained from Shahin-shahr refinery (from site of industrial wastewater) and Zoebahan factory wastewater treatment units and two metal plating factories in Isfahan, Iran. The samples were transferred to laboratory in closed-door bottles and then filtered by Wattman 42 paper to remove any suspended materials. The filtered wastewater then analyzed for EC, pH and some heavy metal concentrations (Table 2). Enough amounts of filtered samples were also kept in fridge (<4 °C) for sorption experiments.

2.4. Chemical treatments of sorbents with base and acid

To modify the sorptive characteristics of rice hull and sawdust, the sorbents were treated with 1 M NaOH and HCl for 4 h at 100 °C on hotplate then washed five times with distilled water. After washing the sorbents were dried at 50 °C in a ventilated oven to reach a constant weight.

[6] Fourier Transformation Infrared Spectroscopy.

2.5. Heat treatment of sorbents

Heat treatment of sorbent samples was done to prepare char in the absence of oxygen. N_2 gas was passed through samples to complete the removal of oxygen. The temperature was 25 °C then slowly increased to 400 °C and was allowed to char for 1 h. Finally the samples were exited from oven after complete cooling.

2.6. Batch sorption experiments

The batch sorption experiments were carried out with 1 g of raw and treated sorbent materials in 100 ml synthetic solutions or wastewater samples. The effect of acid and heat treatments of sorbents on sorption was only studied for Pb(II) and Cd(II). The suspensions in all sorption assays were stirred at 25 °C for 1 h and then filtered through Wattman 42 filters to remove any suspended adsorbent. Initial and final concentrations of metals were determined by atomic absorption spectroscopy (AAS).

2.6.1. The effect of pH on sorption

This experiment was done with synthetic solutions in $C = 10\,mg\,l^{-1}$ and different pHs of 2–7 for all natural and treated sorbents.

2.6.2. The effect of concentration on sorption

This sorption experiment was carried out with synthetic solutions at metal concentrations of 0, 10, 25, 50, 100, 500 and $1000\,mg\,l^{-1}$ in pH 5 for natural, base and heat treated sorbent materials. Sorption data for each metal were fitted to the Langmuir and Freundlich isotherm models.

2.7. Column experiment

The column sorption experiment was done with Zn(II) synthetic solution at pH 5 and $C = 500\,mg\,l^{-1}$ and with plating wastewater. An ion-exchange column W9 series, Armfield, England was used in this study. The column internal diameter was 15 mm and its length was 15 cm. The exchange column filled with 5–10 g of the sorbents and 1 l of metal containing solutions passed through the column in four cycles of 20 min with rate of 50 ml/min. At the end each of sorption courses, the recovery of sorbent was examined by washing the column using distilled water or acid (0.1 M HCl).

2.8. *Comparison test with commercial sorbents*

A batch experiment was done with basic treated rice hull in comparison with granular active carbon and a type of cation-exchange resin (golden granular) using plating wastewater.

2.9. *Statistical analysis*

All treatments were carried out in triplicate. Statistical analysis (Duncan test and ANOVA followed by the Bonferroni method for significance level adjustments due to multiple comparisons) was performed with the computer programs Excel 12.0 and SAS (SPSS Inc., Chicago, IL).

3. Results and discussions

3.1. *Effect of pH on sorption*

Generally removal of heavy metal ions by sorbents was increased with increasing pH from 2 to 7 in synthetic solutions (Fig. 1). The sorption reached to its maximum at pH 5 and then remained almost constant. The increase of pH increases the negative sorption sites and decreases H^+ ion competition with the metal ions for sorption sites, while at higher pHs, the formation of negatively charged hydrolyzed ions decreases again the sorption of metal ions. Based on the results of this work, pH 5 was selected as the lowest pH with highest mean sorption for the most of sorption experiments.

The batch experiments by Rios et al. [4] showed that pH 5 was the best pH for adsorption of most of the metal ions by agricultural by-products. Taty-Costodes et al. [7] have shown the adsorption of heavy metal ions Pb(II) and Cd(II) onto sawdust (of *Pinus sylvestris*) increased with the pH and reached a maximum at a 5.5 value.

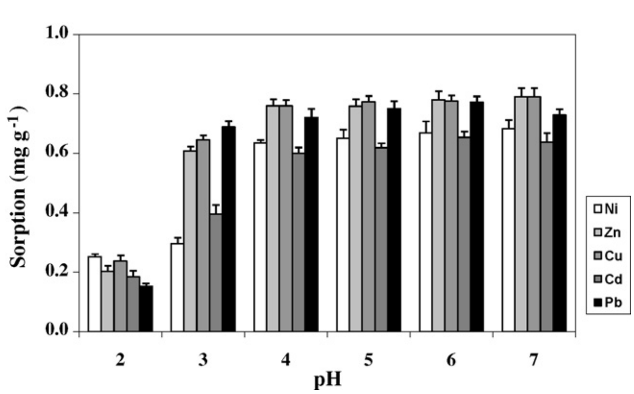

Fig. 1. Effect of pH (2–7) on sorption means of heavy metals by different sorbents (rice hull and saw dust) from synthetic solutions of nickel, zinc, copper, cadmium and lead at $C = 10\,\mathrm{mg\,l^{-1}}$.

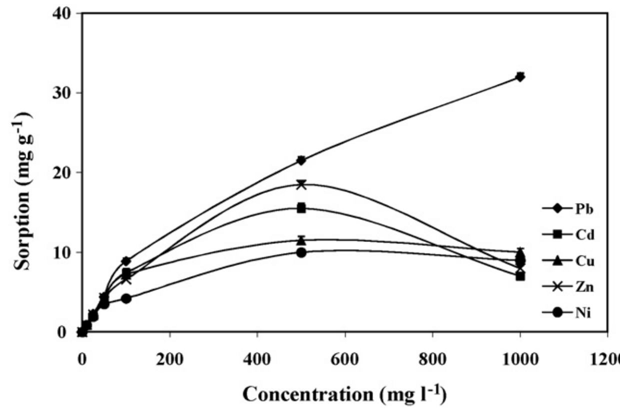

Fig. 2. Effect of initial concentration (0, 10, 25, 50, 100, 500 and 1000 $\mathrm{mg\,l^{-1}}$) of synthetic solutions (nickel, zinc, copper, cadmium and lead) on sorption of heavy metals by basic treated rice hull in pH 5.

3.2. *Effect of concentration on sorption*

At the constant pH, increasing initial concentration of heavy metals ion solutions from 10 to 1000 $\mathrm{mg\,l^{-1}}$, increased sorption of heavy metals by sorbents. This result was observed mostly in raw, base and heat treated sorbents. In case of basic treated samples, for Zn(II), Cd(II), Cu(II) and Ni(II) and in case of heat treated sorbents, for Cd(II), the highest sorption was observed in $C = 500\,\mathrm{mg\,l^{-1}}$ and toward higher concentrations due to probably saturation of sorbent's surface and constant rate of sorbent (1 g) to solution sorption decreased (Figs. 2 and 3). Periasamy and Namasivayam [25] mentioned although with initial concentration increasing weighted sorption increased, but if rate of sorbent to solution was constant due to saturation of sorbent's surface heavy metal sorption decreased from solution in high concentration. The data could be well described by sorption isotherms. The constant and correlation coefficients of these isotherm models were calculated and compared. Based on R^2 values the sorption data were best fitted with Freundlich and Langmuir models for raw and base treatments of rice hull and sawdust expect for Pb, respectively. Data of Pb(II) sorp-

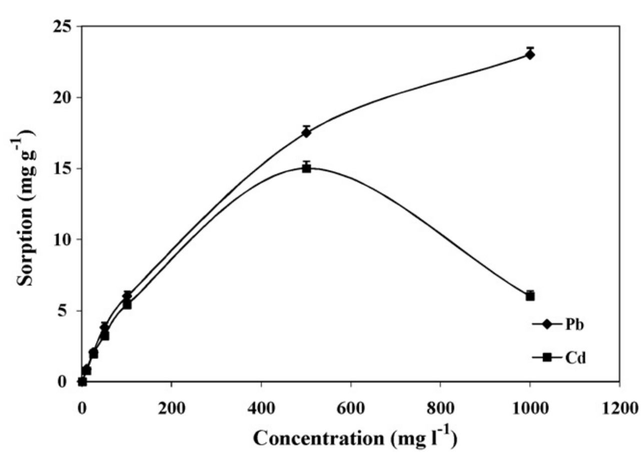

Fig. 3. Effect of initial concentration (0, 10, 25, 50, 100, 500 and 1000 $\mathrm{mg\,l^{-1}}$) of synthetic solutions (nickel, zinc, copper, cadmium and lead) on sorption of heavy metals by heat treated rice hull in pH 5.

tion were fitted by Freundlich model. In case of heat treatment (char samples), data of Pb(II) and Cd(II) sorption were fitted by Freundlich and Langmuir models, respectively. The applicability of Langmuir and Freundlich isotherms showed monolayer and multilayer coverage of adsorbates on the surface of adsorbents, respectively [26]. These different depend on cation's chemical behavior, sorption energy and their affinity to sorbents [12,26,27].

3.3. Modification

Different modification treatments affected the sorptive characteristics of the sorbents. Following, the effects of HCl, NaOH and heat treatments are presented, respectively.

3.3.1. HCl treatment

Acid treatment of sorbent materials decreased Pb(II) and Cd(II) uptake. For Pb(II) and Cd(II), after acid treatment of sawdust and rice hull, the amount of sorption decreased 0.45, 0.61, 0.45 and 0.68 mg g^{-1}, respectively (Table 3). Possibility, decreasing of negative sites and destruction of surface carboxyl groups by acid treatment (results of FTIR) [28] decrease the CEC of sorbents (Table 1). Also the H^+ ion activity that competes with metal ion sorption increases at lower pHs, therefore, the metal ion sorption decreased after HCl treatment. Marshall and Johns [29] showed acid treatment of agricultural by-products such as cotton seed and soybean hull decreased sorption capacity of Zn(II) 78% and 89%, respectively.

3.3.2. NaOH treatment

The base treatment increased the metal sorption of the sorbents (Table 3). The increasing of negative sites and probably addition of surface functional groups during the thermochemical reactions with NaOH also, increasing of CEC and surface area (Table 1), increased the metal sorption capacity of the sorbents.

Acid and base wash inorganic materials such as carbonate and Si from the cell walls of rice hull increases the penetration of N_2 gas to the sorbent surfaces and increases the measured surface area by BET method, however, this increase is not large in comparison with heat treatment. Also, the effect in rice hull was more pronounced than sawdust. This may be due to the higher content of organic carbon in sawdust. Because organic materials do not dissolve in acid or base and their structure is relatively stable with these treatments. Results of FTIR showed that base treatment changed aldeid and aceton OH to hemialdeid and hemiacetal OH, consequently functional groups expose to sorption mechanisms and sorption increased. FTIR spectra of sawdust and rice hull before and after Cu(II) sorption were studied (Fig. 4). Although we cannot exactly say things about sites or quantity sorption of heavy metals by such as spectrums, but the existence of main shifts through spectra after sorption may be reason of sorption. Gaballah et al. [30] showed that the main difference was between FTIR spectrums before and after sorption of Cu(II) on tree barks. Some of the bands shifted after Cu(II) sorption. Laszlo and Dintzis [13] mentioned that occurring of many structural specific changes in sorbents increased sorption of heavy metals after base treatment. Base treatment extracted organic materials such as tannin from sawdust and therefore its sorption efficiency increased [31].

Rios et al. [4] showed that agricultural by-products (wheat biomass) treated with 0.1 M NaOH solution for 30 min had the optimum increase of adsorption capacity for Pb^{2+} and Cu^{2+}. Sciban et al. [32] studied three pre-treatments of sawdust (two types) for modification of sorbents with formaldehyde in acidic medium, sodium hydroxide solution after formaldehyde

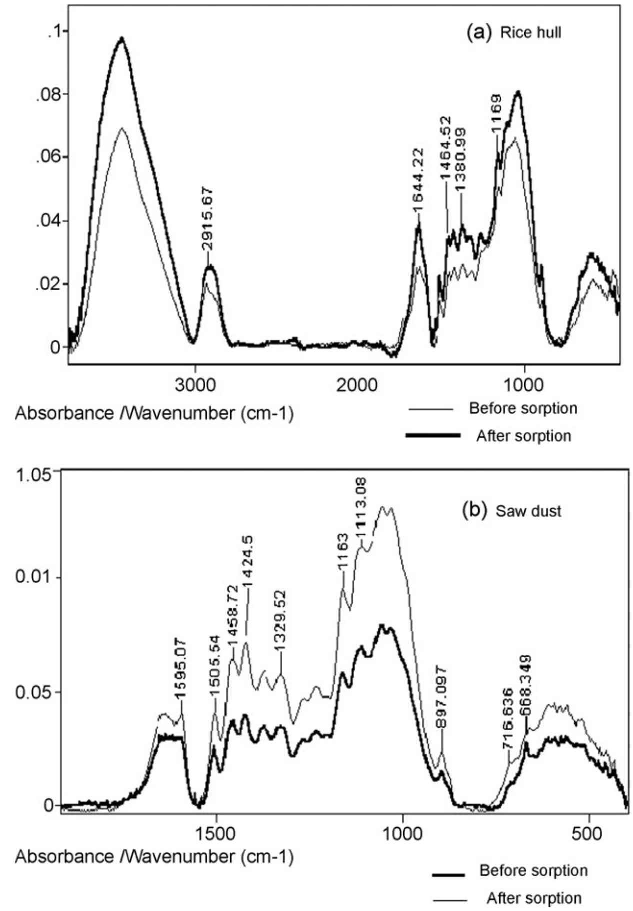

Fig. 4. FTIR spectrum of treated sorbents (rice hull and sawdust) before and after sorption of Cu(II). The existence of main shifts through spectra after sorption may be reason of sorption. FTIR spectrums are different before and after sorption of metal ions on sorbent materials.

Table 3
Comparison of heavy metals sorption (mg g^{-1}) by different treated sorbents in pH 5 and $C = 10$ mg l^{-1}

Sorbent	Treatment	Pb(II)	Cd(II)	Cu(II)	Zn(II)	Ni(II)
Sawdust	Raw	0.82^{a}	0.74^{a}	0.69^{b}	0.62^{b}	0.49^{b}
	Base	0.89^{a}	0.84^{a}	0.80^{a}	0.82^{a}	0.66^{a}
	Heat	0.86^{a}	0.79^{a}	–	–	–
	Acid	0.37^{b}	0.13^{b}	–	–	–
Rice hull	Raw	0.84^{ab}	0.80^{a}	0.68^{b}	0.70^{b}	0.57^{b}
	Base	0.95^{a}	0.89^{a}	0.92^{a}	0.89^{a}	0.88^{a}
	Heat	0.87^{ab}	0.83^{a}	–	–	–
	Acid	0.39^{b}	0.12^{b}	–	–	–

Means marked with the same character, for each sorbent and a given metal, are not have significantly ($p < 0.01$) different.

treatment, and sodium hydroxide only. The studies indicated when formaldehyde was applied for modification, the adsorption capacities of adsorbents remained unchanged. Only the application of sodium hydroxide was recommended for modification of hardwood sawdust. Extracting fibers with different solvents will change both chemical and physical properties of the fibers. It is known, for example, that during the hot water and 1% sodium hydroxide extraction of fibers, the cell walls delaminate. At the same time, some of the amorphous matrix and part of the extractives, which have a bulking effect, are removed, so that the individual micro fibrils become more closely packed and shrunken. Therefore, delamination and shrinkage may also change the amount of exposed lignin and other cell wall components that may affect the heavy metal ion sorption capacities of the fibers. Each different extraction chemical will swell lignocellulose materials to a different extent, thus removing different amounts and types of extractives as well as cell wall components [33].

Increasing of pH and initial concentration of solution increased sorption by base treatment (Figs. 1 and 2). The uptake increase after base treatment was different for each metal. This difference was lower for heavier metals as Pb(II) and Cd(II) than other metals. For Zn(II) and Ni(II), after base treatment of sawdust and rice hull, the amount of sorption increased 0.2, 0.17, 0.19 and 0.31 mg g^{-1}, respectively (Table 3).

3.3.3. Heat treatment

Active carbon process by heat in anaerobic system changed sorbent materials to char, consequently, increasing of surface area (Table 1) increased sorption of heavy metals. Structure of rice hull is destroyed by heat and converted to very small particles of carbon but about sawdust because of high rate of organic materials (such as lignocellulos), the particles of pure carbon are in forms of granular and large in size. Therefore, the surface area of heat treated rice hull was 100 times as much as the raw rice hull, while this rate was 15 in sawdust. A cubic of 1 ft of activated carbon particles might have 10 mile −2 of surface area [34]. However, a pour surface of carbon is supposed non-polar, but truly, complexes as C_xO_2, C_xO and CO_x cause a low polar surface. There is no strong method to determine the amount of this charge. Way of ions uptake by this complexes is ion-exchange [25].

In heat treatment, also, increasing pH, increased sorption and maximized in pH 4–6 (Fig. 1). In pH 5, sorption did not show remarkable increase rather than raw materials (Table 3), but in lower pH (pH 3–4) heat treatment of sawdust increased the Cd(II) sorption 0.1–0.14 mg g^{-1}. Increasing of initial concentration of solution increased sorption of Pb(II) and Cd(II) by heat treatment (Fig. 3). Namasivayam and Kadirvelu [35] showed that maximum Cu(II) adsorption on active carbon of agricultural by-products occurred in pH 5–6. In this pH, Cu^{2+} is hydrolyzed to $Cu(OH)^+$ and then $Cu(OH)_2$. Non-polar species such as $Cu(OH)_2$ are adsorbed more than polar species on non-polar surface of active carbon. Kim and Choi [34] showed high sorption of Cd(II) and Pb(II) by active carbon of rice hull.

Table 4
Means of heavy metals sorption (mg g^{-1}) on sorbents

Sorbent	Pb(II)	Cd(II)	Cu(II)	Zn(II)	Ni(II)
Sawdust	0.76^a	0.63^b	0.65^a	0.62^b	0.45^b
Rice hull	0.76^a	0.74^a	0.67^a	0.68^a	0.60^a

Each data is mean of different pHs (2–7) in $C = 10$ mg l^{-1}. Means marked with the same character, are not have significantly ($p < 0.01$) different.

Comparison of all treatments that was done for Pb(II) and Cd(II) was in this manner: basic > char > raw > acidic. In pH 5, maximum of sorption belonged to Pb(II) and Cd(II) in base treatment of rice hull with means of 0.95 and 0.89 mg g^{-1}, respectively (Table 3). Marshall and Johns [29] mentioned at pH 6–7 for basic treated sawdust, sorption amount of Cd(II), Cu(II), Zn(II), Ni(II) and Pb(II) was 0.72, 0.86, 0.83, 0.84 and 0.89 mg g^{-1} and for basic treated rice hull was 0.9, 0.9, 0.89, 0.89 and 0.9 mg g^{-1}, respectively. Other studies showed the capacity of the metal ions to bind onto organic sorbents (sawdust, rice husk, etc.) was 96% for Cd^{2+}, 98% for Pb^{2+} and 43.6% for Cu^{2+} [7,8].

In comparison with sorbents, the highest sorption capacity of most heavy metals expected Cu(II) was observed for the rice hull followed by sawdust (Table 4). The higher sorption capacity of rice hull than sawdust for removal of heavy metals is probably due to the presence of silanol (SiOH) groups in structure of rice hull, high Si% and more surface area of rice hull (Table 1). Difference between sorbents for Cd(II), Zn(II) and Ni(II), significantly ($p < 0.01$) but for Pb(II) and Cu(II) was not significant (Table 4). Cation's behavior is different toward sorbents and treatments. Also, effect of pH and concentration on this behavior is different. Example, at pH 5 and $C = 10$ mg l^{-1}, among the heavy metals and treated or raw sorbents, Pb(II) showed the highest sorption, followed by Cd(II), Cu(II), Zn(II) and Ni(II), respectively (Table 3). Difference in sorption of heavy metals by sorbent materials depends probably on the affinity of metal ions for active groups on the substrate. Of course, if amount of sorption is expressed in centimole charge on kilogram ($cmol_c$ kg^{-1}) and truly heaviness of metal ion is ignored, uptake amount of heavier metal ions as Pb(II) and Cd(II) is less than Zn(II) and Cu(II). In sawdust maximum of sorption observed for Cu(II) and by rice hull maximum sorption occurred for Zn(II) and Cu(II). Also sorption of Cu(II) was higher on sawdust (3.12 $cmol_c$ kg^{-1}) as compared with rice hull (2.10 $cmol_c$ kg^{-1}). This shows that Cu(II) forms especial complexes with surface functional groups of sawdust.

Following the synthetic solution experiments, wastewater refinement was examined with rice hull and sawdust.

3.4. Shahin-shahr wastewater

The heavy metals concentration of this wastewater except Ni(II), is in the standard range of Iran Environment Organization. However, decreasing of heavy metals concentration can improve the quality of wastewater hogwash. The basic treated rice hull and sawdust sorbed the maximum ion metals. Rice hull and sawdust char sorbed the maximum Ni(II). In case of Cu(II), basic treated sawdust, basic treated rice hull and rice hull char and for

Pb(II) and Zn(II), basic treated rice hull showed the maximum sorption, respectively.

3.5. Zoebahan wastewater

The concentration of the metals Pb(II), Cu(II), Zn(II), Ni(II) and Fe(II) is in the standard range of Iran Environment Organization, however, application of this sorbents can help to a complete refinement of this wastewater. The Cd(II) concentration is below detection limit. In general, basic treated sawdust and rice hull sorbed the maximum amount of ions.

3.6. Plating wastewater

In metal plating wastewater the pH that was 13.9, maximum metals uptake occurred on basic treated rice hull. Also, Zn(II) and Cu(II) uptake by basic treated sawdust was high probably due to formation of strong complexes of Cu(II) and Zn(II) with functional groups of sawdust surface. This wastewater is a by-product of Zn(II) and Cu(II) plating, therefore, Zn(II) concentration is very high. Hence maximum uptake by all sorbents observed for Zn(II). Basic treated rice hull and sawdust sorbed 68.4 and 64.3 mg g^{-1}, respectively. Rice hull char, sawdust char, acidic treated rice hull, acidic treated sawdust, raw rice hull and raw sawdust sorbed 57.6, 55.9, 42.4, 36.3, 32.3 and 22 mg g^{-1} of Zn(II), respectively.

3.7. Column experiment

3.7.1. Column experiment by synthetic solutions

In column test, basic treated rice hull and basic treated sawdust sorbed 98.5 and 89.7 mg g^{-1} Zn(II), respectively. In comparison with suspension method that amount of Zn(II) uptake by basic treated rice hull and sawdust (in pH 5 and C = 500 mg l^{-1}) was 18.5 and 15.5 mg g^{-1}, respectively, application of sorbents as column shows higher amount of uptake.

3.7.2. Column experiment by wastewater

In this experiment 1 l of plating wastewater containing Zn(II), Cu(II), Cd(II), Ni(II), Fe(II) and Pb(II) passed through basic treated rice hull and sawdust columns. Concentration of Zn(II) and Fe(II) was very high in the wastewater, therefore the highest uptake was occurred. In comparison between basic treated rice hull and sawdust, with low difference, basic treated rice hull showed higher uptake. Basic treated rice hull and sawdust sorbed 232, 229, 56.9 and 40.9 mg g^{-1} Fe(II) and Zn(II), respectively. But for Cu(II), basic treated rice hull and sawdust sorbed the same amount of 1.32 mg g^{-1}.

de Matos et al. [8] used columns of organic filter for removal of Cu(II) and Zn(II) from waste water. Each filtering material was placed in a 100 mm diameter, 600 mm long, PVC column to a height of 500 mm under 12500 N m^{-2} of compression. Chemical and physical analyses were determined on effluent samples collected for each 1.5 l up to a total of 15 l. The organic materials reduced the concentration of sediment solids (>90%), total solids (up to 33%) and Cu(II) (up to 43.6%) of the influent but had little or no effect on Zn(II) concentration.

3.7.3. Column recovery

Metal ions which are bound to the by-product agricultural sorbents could be stripped by acidic solutions (dilute hydrochloric or nitric acid) so that the sorbents can be recycled [6,24].

In this study, column of rice hull was completely recovered after passing wastewater by 1 l water and then 1 l acid (HCl 0.1 M). To study the efficiency of sorbents after recovery, the same wastewater was passed through the column again. Sorption of column did not decrease so much after recovery therefore these sorbents may be used for more cycles of sorption and recovery. Cu(II) was an exception and its sorption decreased strongly after acid washing of column, probably due to formation of especial complexes of Cu(II) with functional groups. In case of Zn(II), 47.3% and 33% is recovered by water and acid, respectively. Recovered Ni(II), Pb(II), Fe(II) and Cu(II) by water was 60%, 23.1%, 10% and 7% and recovered by acid was 67.7%, 100%, 16.8% and 2.3%, respectively. Sometimes, the amount of recovered ion is higher than the sorbed metal ion that could be due to washing of remained wastewater in course and pipes.

Zhou et al. [36] studied the ability of the cellulose fixed-bed column to adsorb Pb^{2+} from an aqueous solution. The columns were easily regenerated by treating with 0.1 M HCl aqueous solution after the adsorption of metals, providing a simple and economical method for removal and recovery of heavy metals. After four adsorption–desorption cycles, the efficiency of column for the removal of Pb^{2+} was not significantly reduced (not more than 5%). It is shown that heavy metal biosorption processes in fixed-bed columns could give a broad range of potential industrial applications. Shukla and Roshan [20] in removal of Pb(II) from solution using cellulose-containing materials showed in repeated adsorption–desorption cycles, with an intermediate step of mild sodium hydroxide treatment, sorbent materials retained its adsorptive capacity even after five cycles of re-use.

3.8. Comparative experiment using commercial sorbents

In this test, the sorption behavior of basic treated rice hull was compared with active carbon and a kind of by-product exchange resin using plating wastewater. Although the amount of sorption by commercial sorbents was higher than rice hull for Pb(II), Cd(II), Zn(II) and Fe(II), but sorption of basic treated rice hull was very remarkable especially for Zn(II). Also, for Cu(II), rice hull, because of formation of especial complexes with surface functional groups, showed higher efficiency than active carbon and resin (Table 5).

Table 5
Heavy metals concentration (mg l^{-1}) in plating wastewater before and after implication of different sorbents

Treatment	Pb(II)	Cd(II)	Cu(II)	Zn(II)	Ni(II)	Fe(II)
Initial wastewater	1.00	1.00	15.00	1114	3.02	3000
Basic rice hull	0.53	0.33	7.06	660	2.09	2610
Resin	0.38	0.30	13.36	603	2.16	2550
Active carbon	0.31	0.30	13.40	580	2.01	294

Marshall and Champagne [12] showed that effect of modified rice hull for removal of Cu(II) and Zn(II) from wastewater was equal to commercial resin (IRC_718).

4. Conclusions

Agricultural by-product materials or modified natural polymers appear as effective and cheap sorbents for removal of heavy metals from wastewater. Moreover, the materials could also be used for purification of water. The removal of metal ions from effluents is important to many countries of the world both environmentally and for water re-use. The sorption capacity of rice hull was more than sawdust. As a modification process, the base treatment of sorbents showed the highest efficiency. These sorbents can use for several cycles of sorption and recovery in column systems. Low cost biosorbents are valuable alternatives for commercial sorbents.

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