

# Removal of Heavy Metals from Aqueous Solutions by Natural Adsorbents (A Review)

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## A-R-T-I-C-L-E I-N-F-O

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## A-B-S-T-R-A-C-T

**Background & Aims of the Study:** The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. The removal of pollutants from water and wastewater is a problem that has grown with rapid industrialization. The discharge of toxic metals into watercourses is a serious pollution problem, which may affect the quality of water supply. By confirming the toxic effects of these metals, various methods have been implemented to remove pollutants from aqueous solutions. The aim of this study was determining the removal efficiency of natural adsorbents for removing heavy metals from aquatic solutions.

**Materials & Methods:** In this review study, 39 experiments from 23 published papers on the mentioned topic between 2000 and 2011 were selected and the effective parameters on removal efficiency were studied and concluded.

**Results:** The average removal efficiency was 88.14%. In more than 65% of studies the removal efficiency was above 90%. In more than 96% of experiments, by increasing the adsorbent dose, the removal of heavy metals increased. Average optimum pH for maximum adsorption of heavy metal ions was 5.47, and the removal efficiency at acidic pH was allocated 76.92%. Twenty four experiments have examined the effect of contact time on the removal efficiency, which with increasing time to reach equilibrium time, the removal efficiency increased. In 16 studies, primary concentration was investigated, which by increasing concentrations of heavy metals, removal efficiency decreased. 58.97% of data were compatible with Langmuir isotherm.

**Conclusions:** According to the results, sawdust can be used as a low cost, natural and abundant availability adsorbent for removal of heavy metal ions from aqueous solution.

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## Background

Water resources pollution due to the disposal of heavy metals has been an increasing worldwide concern in the last few decades. The problem of removing pollutants from water and wastewater has grown by rapid industrialization. The discharge of toxic metals into watercourses is a serious pollution problem, which may affect the quality of water supplies. Release of these metals to surface water and groundwater is done by industries such as metallurgical, mining, chemical, tannery, jewelry, electrical, smelters, electroplating, dyes, textiles, oil refineries, pulp and paper production, metal plating facilities, mining operations, battery manufacturing processes, production of paints and pigments, glass production, ceramics, fungicides, rubber, fertilizers, and aircraft industry (1-4). The problems of the removal of these pollutants have increased by industrialization of countries and unsanitary disposal of wastewater. These metals even are present in storm water runoffs from urban and agricultural areas and cause health problems in animals, plants, and human beings (3). These metals are (Cd), (Hg), (Pb), (Cu), (Cr), (Ni), (Zn), (As), (Co), (Ag), (Au), (Se), (V), (Sb), (Bi), (Mn), (Ce), (Ga), (Pt), and (Fe) (4-6). For example, excessive human intake of Cu causes severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal injury, and central nervous system irritation followed by depression. Severe gastrointestinal irritation and possible necrotic changes in the liver and kidney can also happen. Nevertheless, copper has lots of commercial uses. It is used for making pipes, valves, and fittings and also is present in coating sand alloys that sometimes for algae control in surface water, copper sulfate pentahydrate is added it (1). Guideline value for this metal is 2 mg/L (5). Unfortunately, copper components may increase during the water distribution because of the acidic or alkaline pH

(5). Another heavy metal which is called inorganic mercury has a guideline value of 0.006 mg/liter for drinking water. This metal is used in electrolytic production of chlorine, in dental amalgams, and also in electrical appliances. The next element, which is found in the earth's crust, is named chromium; there are two forms of chromium: trivalent [Cr (III)] and hexavalent chromium [Cr (VI)] (1,7). Hexavalent chromium is known as a strong oxidant and highly toxic for healthy body. Provisional guideline for total chromium is 0.05 mg/L (5). Nickel (Ni) is another heavy metal, which is applied in the production of stainless steel and nickel alloys, and its guideline value is 0.07 mg/L. The effects of Ni exposure vary from skin irritation to damage to the lungs, nervous system, and mucous membranes (5). Arsenic in drinking water is a major cause of health effects, which is considered to be a high-priority substance for screening in drinking water sources. Depending on well depth, concentrations are various. Its provisional guideline is 0.01 mg/L (5). Lead is a common industrial metal that exists widespread in air, water, soil, and food; it is used in abundance for the production of lead-acid batteries, solder, and alloys, as well as the organolead compounds, such as tetraethyl lead and tetramethyl lead that are extensively applied as antiknock and lubricating agents in petrol (5). Lead is rarely present in natural water sources due to dissolution from household plumbing systems containing lead (including solder, pipes and fittings). It should be considered that the amount of dissolved lead from the plumbing system depends on several factors, including pH, temperature, water hardness, and water detention time; lead's guideline level has been determined 0.01 mg/liter by WHO (8). The most practical uses of lead in the United States are in storage batteries (72%), gasoline additives and other chemicals (13%), ammunition: shot and bullets (4%), solder (2%), and other uses (9%). Its worldwide production has exceeded from 3

million tons per year. Unfortunately, lead causes severe health problems even at relatively low levels in the body, for example irreversible brain damage and injury to the blood-forming systems. At the typical levels, lead can cross the placenta and damage developing fetal nervous systems (8). Cadmium is another heavy metal which is released to the environment and diffuses pollution caused by contamination from fertilizers and local air pollution. Contamination in drinking water may be caused by impurities in the zinc of galvanized pipes and solders and some metal fitting, and its guideline value is 0.003 mg/liter in drinking water (5). The next metal is tin, which is principally used in the food industry as a corrosion inhibitor. Fortunately, drinking water is not a significant source of tin, No evidence presents that this metal cause carcinogenic effects in the long-term. Studies have shown that tin has no teratogenic or fetotoxic effects in mice, rats, or hamsters. Iron is a vital element that is called heavy metal that is nutrition for body. Minimum daily requirement for iron depend on sex, age, physiological status, and iron bioavailability, with a range of 10 to 50 mg/day. Iron may also be present in drinking water because of the use of iron coagulants or the corrosion of steel and cast iron pipes during water distribution (5). By confirming the toxic effects of heavy metals on humans and the environment, various methods for removal of these metals from water and wastewater are examined, such as chemical and electrochemical precipitation, coagulation and flocculation, complexation/sequestration, biological treatment, electrochemical deposition, ion exchange resins, reverse osmosis, solvent extraction, membrane filtration, oxidation, cementation and adsorption on adsorbents. These methods do not seem to be economical and in huge scales, most of the removal methods are cost-effective only for relatively low concentrations of heavy metals (1-4,9,10), For example, ion-exchange has the advantage of allowing the recovery of

metallic ions, but it is costly and complicated (11), therefore, chemical and electrochemical precipitation becomes more prevalent (2), but precipitation methods requires large settling tanks for precipitation of huge alkaline sludges and a further treatment is needed. pH should be controlled at coagulation process (11), that requires more investment and high costs operating (1,10), also, chemical precipitation is not suitable for removing low concentration of heavy metal ions (1). So, it becomes essential to investigate a low-cost method which is effective, economic, and can be used by such industries. Adsorption, as compared to other methods, seems to be a simple attractive process due to its high efficiency, easy handling and cost-effectiveness, and also due to the availability of different adsorbents. In addition, advantages, such as recovery of metal and reuse of the adsorbent can be added to this method (6). Treatment of the water and wastewater is done using synthetic and natural adsorbents, because the process of adsorption implies an 'adsorbent' which can efficiently binds molecules by physical attractive forces, ion exchange, or chemical binding (10). The first quantitative studies were reported by Scheele in 1773 on the uptake of gases by charcoal and clays. This study was followed by Lowitz's observations that used charcoal as an adsorbent to decolorize tartaric acid solutions. Larvitz and Kehl observed similar phenomenon with vegetable and animal charcoal in 1792 and 1793, respectively. However, the term "adsorption" was widely used for the removal of solutes from solutions and gases from air atmosphere (9). There are a lot of adsorbents for removal and reduction of pollutants from environmental waters, that among different adsorbents, activated carbon can apply for removal of numerous trace elements from water and wastewater with high efficiency, but it is not cost-effective for large-scale use (10).

If the adsorption process is selected with selective adsorbents, adsorption on natural

elements can play an important role to separation them from water systems (2,6). By-products and wastes from agricultural and forest industries are materials that could be assumed as low-cost since they require little processing and are abundant in nature (10,12). For example, sawdust (SD) is a waste by-product of the timber industry that is produced in large quantities and used as cooking fuel, packing material, and for making and heating in the boilers (2,10).

Various chemical treatments of sawdust can improve the heavy metal binding capacity of this material (10,13). Several natural adsorbents, including bark of trees (14), agricultural waste (15,16), powder of poplar leaves and branches (17), rice bran (18), sawdust (19), orange peel and bagasse (20), green algae (21), soybean and cottonseed hulls, hazelnut shell, sugar beet pulp, peat moss, activated carbon fibers, coconut waste, straw, olive stone, fly ash, biomass, cactus waste, and humic acids (1,2,9,10) have been investigated for their ability to sequester metal ion from water. Adsorption capacity depends on the nature of adsorbent, their porosity, and large surface area with more specific adsorption sites. The porous structure not only increase surface area and consequently adsorption, but also the kinetics of the adsorption and requires less time to reach equilibrium adsorption (9). There are three types of adsorption: chemical, physical, and electrostatic, but the most adsorption in the environmental waters is physical type (22).

In this review study, the removal efficiency of heavy metal from aquatic solution and the effective parameters on this phenomenon by natural adsorbents have been investigated and concluded.

## Materials & Methods

In the current study, 39 experiments from the 23 published papers with the title "removal of

heavy metals from aqueous solutions by natural adsorbents" between 2000 and 2011 were randomly selected and the effective parameters on removal efficiency were investigated. These papers were searched among the network pages and presented references in the papers. The applied keywords for searching were: removal, aquatic solutions, heavy metals, and sawdust. Because of allocating more than 90% of experiments to batch system, in the present study, the removal of heavy metals from aquatic solution by this system has been investigated in different studies.

## Results & Discussion

### Information about the investigated studies

Table 1) Data from various studies with the subject "removal of heavy metals from aqueous solutions by sawdust"

	Adsorbent	Heavy Metal	Removal Efficacy (%)	pH	Adsorption capacity (mg/g)	contact time (min)	Dose (g/l)	Initial concentration (mg/l)	Reference
1	sawdust	Cu(II)	95	5.5	5.2	120	20	200	(22)
2	Red Pine sawdust	Cr(VI)	55.2	3	5.5	120	3.33	-	(10)
3	Red Pine sawdust (BESD)	Cr(VI)	70.6	3	10.10	120	3.33	-	(10)
4	Red Pine sawdust (TASD)	Cr(VI)	87.7	3	10.72	120	3.33	-	(10)
5	Oak sawdust	Cu(II)	93	4	3.22	240	40	0.1-150	(1)
6	Oak sawdust	Ni(II)	82	8	3.29	480	30	0.1-150	(1)
7	Oak sawdust	Cr(VI)	84	3	1.7	480	60	0.1-150	(1)
8	Acacia arabica sawdust	Cr(VI)	99.3	6	111.6	75	10	3	(6)
9	Acacia arabica sawdust	Hg(II)	94.6	6	52.38	75	10	3	(6)
10	Acacia arabica sawdust	Pb(II)	99.4	6	20.62	75	10	3	(6)
11	Acacia arabica sawdust	Cu(II)	92.2	6	5.64	75	10	3	(6)
12	Meranti sawdust	Cu(II)	89	6	32.051	120	10	100	(2)
13	Meranti sawdust	Ni(II)	97	6	35.971	120	10	100	(2)
14	Meranti sawdust	Cr(III)	94	6	37.87	120	10	100	(2)
15	Meranti sawdust	Pb(II)	99	6	32.246	120	10	100	(2)
16	sawdust	Cr(VI)	99.6	7	3.7	80	1	1	(21)
17	poplar sawdust	Cu(II)	92.38	5	13.495	60	5	50	(23)
18	poplar sawdust	Cu(II)	47.05	4	5.432	60	5	50	(23)
19	Maple sawdust	Pb(II)	98.8	5	3.19	360	40	10	(8)
20	Maple sawdust	Cu(II)	95	7	1.79	360	40	10	(8)
21	sawdust	Cr(VI)	62.2	3	25.4-9.2	180	25	100	(24)
22	sawdust (SDC)	Cr(VI)	86.6	3	3.7-10	60	25	100	(24)
23	Hevea Brasilinesis sawdust	Cr(VI)	-	2	44.05	300	2	2000	(25)
24	Pinus sylvestris sawdust	Cd(II)	96.2	5.5	95	60	0.1	10	(26)
25	Pinus sylvestris sawdust	Pb(II)	97.5	5.5	98	60	0.1	10	(26)
26	Holly sawdust	Ni(II)	99.98	7	22.47	240	6	60	(27)
27	sawdust	Pb(II)	90	6.5	-	240	2	-	(28)
28	Palm sawdust	Cr(VI)	94	4	-	180	40	20	(29)
29	sawdust	Cu(II)	94	7	1.79	180	10	10	(30)
30	Pinus sylvestris sawdust	V	95	4	-	160	50	-	(3)
31	Pinus sylvestris sawdust	Pb(II)	99	4	-	160	50	-	(3)
32	Heveasawdust	Zn(II)	73.39	6	-	240	2	40	(31)
33	Heveasawdust	Ni(II)	69.21	6	-	240	2	40	(31)
34	maplesawdust	Cr(VI)	83	9	-	60	50	10	(32)
35	Holly sawdust	Cr(VI)	99.76	7	18.86	180	6	60	(12)
36	sawdust	Pb(II)	55	6	18	120	2	25	(33)
37	Pinus Halepensis sawdust	Cd(II)	100	9	5.36	30	20	5	(23)
38	sawdust (EDTA)	Cu(II)	98	6.4	3.12	50	10	-	(19)
39	sawdust (EDTA)	Zn(II)	92	7	80	60	1.2	200	(34)

**The efficiency of heavy metals removal**  
 According to table (1), in 38 out of 39 experiments, the removal efficiency of heavy

metal had determined that the optimum average efficiency obtained 88.14%, and in more than 65% of studies the removal efficiency obtained above 90%, that the most removal efficiency of heavy metals was allocated to Ni and Cr using holly sawdust (13,27). Shirzad *et al.* have obtained removal of Cr (VI) with natural and synthetic adsorbent, respectively, 94.41% and 99.76% that is indicative of high capability of sawdust, which is the same as synthetic adsorbents for removal of heavy metals (13,34). Removal efficiency depends on several parameters, such as pH, adsorbent dosage, initial concentration of metal ions, temperature, contact time, and shaking speed, that we have discussed these factors.

#### **The effect of adsorbent dose on removal efficiency**

Among 39 studied experiments, in 30 experiments, the effect of adsorbent dose on removal efficiency of heavy metal had demonstrated that in more than 96% of experiments, removal of heavy metals from aquatic solution increased by increasing the adsorbent dose. In a study, by increasing adsorbent dose from 0.2 g to 1 g, the removal efficiency increased from 34.65% to 99.99% (27). Also, in other studies, the removal efficiency of ions increased with increasing adsorbent mass (2,3,29,33). Adsorption of copper increased by increasing adsorbent dose that can be attributed to increased surface area and availability of more adsorption sites (23). In Suresh Gupta *et al.*'s study, removal efficiency of Cr (VI) was increased from 59.4% to 74.6% with an increase in the adsorbent mass from 15 to 30 g that can be attributed to increase of the adsorbent surface, which provides more binding sites for the adsorption (35). Biosorbents usually have organic functional groups, such as alcohol, aldehydes, ketones, carboxylic, phenolic, and ether groups on their surface. These groups have been shown to participate in cation binding due to their ability to ionize in aqueous solution (36,37).

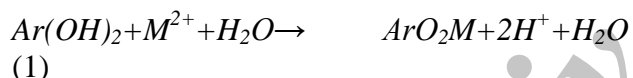
Cell wall of such these adsorbents is mainly consists of cellulose, hemicelluloses, and many hydroxyl groups such as tannins and lignin. Lignin is the third major component of the wood that is usually in the range of 18–35% and is built up from the phenylpropane nucleus; an aromatic ring with a three carbon side chain is promptly available to interact with cationic metal ions (2,10,30,31). Tannins are complex polyhydric phenols which exist mainly in hardwoods. All those components are active ion exchange compounds (10).

#### **The effect of pH on removal efficiency**

pH is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions. According to Table1, the average optimum pH for maximum adsorption of heavy metal ions in 39 experiments was calculated 5.47 and maximum removal efficiency at acidic pH was allocated 76.92%. Removal efficiency for natural pH was obtained 15.38% and minimum removal efficiency was 7.69%. In the studies, the percentage adsorption increased with increasing pH to reach a maximum at pH 6 and then, it decreased with further increase in pH (26). In a research by Kaczala *et al.* a significant increase in the removal efficiency from 32% to 99% for lead (Pb) and from 43% to 95% for vanadium (V) was observed when the initial pH was reduced from 7.4 to 4.0 (3). The possible sites on sawdust for specific adsorption includes hydrogen ions in carboxyl and hydroxide functional groups in which H<sup>+</sup> ions can be exchanged for cations in solution; other sites on the modified sawdust can also contribute to the adsorption process (6). Bin Yu *et al.* attained maximum removal of pb(II) and chromium at pH=5 (8,29). Also, maximum adsorption of Cd(II) and Pb(II) was at pH=5 (6). The results of Shirzad *et al.*'s study showed that by increasing pH from 3 to 5, removal efficiency increases from 77.8% to 80.4% and at pH 11 reached 20.4% (38). In acidic medium, the electromeric effect of the amide group in

sawdust cause surface protonation and possesses net positive charge on the surface. These hydrogen ions from the surface can be exchanged with positively charged adsorbate species with subsequent coordination of a metal ion. An increase in pH shows a slight increase in adsorption, in which the surface of the adsorbent is negatively charged and the adsorbate species are still positively charged. The adsorbent surface is negatively charged in addition to the increasing electrostatic attraction of metal ions. Decrease in removal of metal ions at lower pH is seemed to be due to the higher concentration of hydrogen ions that are present in the reaction mixture and compete with the  $M^{2+}$  ions for the adsorption sites of sawdust. Decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes that lead to less efficiency (6,9,10,30).

Reaction adsorption of heavy metal in aquatic solution:



Where Ar is a functional group of the modified sawdust, such as the carboxylic groups of polysaccharides, the phenolic groups of lignin, and hemicellulosic material, and M represents metal ions (1).

#### **The effect of contact time on removal efficiency**

Twenty-four out of 39 experiments had investigated the effect of contact time on removal efficiency, which in the all of them the percent removal of heavy metal increases by increase of contact time till equilibrium is attained. Shirzad et al. by varying contact time from 5 to 180 min at natural pH, sawdust dose of 6 g/L and initial Cr (VI) concentration of 60 mg/L, improved the removal efficiency from 48.53% to 99.76% (13). The removal of Cu (II) ions is high in the first 10 min and then, the rate significantly decreases and eventually approaches zero, and finally the equilibrium point has been attained (24). For a fixed

concentration of heavy metals and a fixed adsorbent mass, the rate of heavy metals adsorption at initial times of experiment is high due to more availability of areas. By increasing contact time, the removal efficiency is increased (38,39,40), because contact time between adsorbent and adsorbate and reaching to adsorption sites are increased. A similar result has been found by other researchers (1,23). The removal efficiencies decreased by approximately 4–10% with increasing contact time following equilibrium had been reached. This probably resulted from saturation of adsorbent surfaces with heavy metals followed by adsorption and desorption processes that occur after saturation (1).

#### **The effect of initial concentration on removal efficiency**

Among 39 experiments, 16 studies had investigated the effect of initial concentration on removal efficiency that their results showed that by increasing initial concentration of heavy metal, the removal efficiency decreased. Also, 10 experiments had investigated the adsorption capacity of adsorbent, that their results revealed that by increasing initial concentration of heavy metal, the amount of heavy metal ions adsorbed per unit mass of adsorbent increased.

The percentage of Cr (VI) removal decreased from 99.37 to 40.24% by increasing the initial Cr (VI) concentration from 20 to 100 mg/L. The decrease in the percentage removal can be explained by the fact that the adsorbent had a limited number of active sites, which would have become saturated above a certain concentration (27). With enhancing initial concentration of Cr (VI), its uptake was reduced for sawdust carbon from 99.8% to 74.8% and for sawdust from 87.8% to 36.2% as concentration was increased from 25 to 200 mg/L (25). The equilibrium sorption capacity of the biomass for Cd (II) and Pb (II) ions increased with rise in the initial ions concentration (11). An increase in the Cd concentration from 1 to 50 mg/L results in a

decrease in the percent metal removal from 100% to 87% and an increase in adsorption capacity from 0.11 to 5.36 mg/g. The decrease in the percentage removal of Cd can be attributed to saturation of available active sites on the adsorbent above a certain concentration of metal. The increase in adsorption capacity may be because of the greater adsorption rate and the use of all available active adsorption sites at higher metal concentration (41).

### **The effect of agitation speed on removal efficiency**

Because shaking consumes energy and affects the adsorption efficiency, it is important to determine the optimal speed. Agitation affects adsorbate dispersal in aquatic solution (23). The average optimal agitation speed was obtained 363 rpm in 32 experiments. In Argun *et al.*'s study, adsorption values for the Cu, Ni, and Cr ions were lowest at 100 rpm and increased as the shaking speed increased to 250 rpm, then decreased slightly as speed increased to 450 rpm. This effect can probably be associated with the decrease in boundary layer thickness around the adsorbent particles due to increasing the degree of mixing. When the mixture was shaken, the solid particles moved around rapidly in the solution (1). Increasing the agitation speed, improved the diffusion of Cr ions towards the surface of the adsorbents. A shaking rate in the range of 100-200 rpm is adequate to ensure that all the surface binding sites are made readily available for Cr uptake. Agitation speed of 150 rpm was selected as the optimum speed for all the adsorbents (29).

### **Adsorption isotherms**

The equilibrium sorption isotherm is fundamentally important in designing sorption systems. Among 39 experiments, 58.97% of data had been accorded with Langmuir isotherm, 23.07% with Freundlich isotherm, 10.25% with Temkin and urami model, and 7.69% with both of Langmuir and Freundlich. According to the results of Agoubordea and

Naviab, data of adsorption of Zn (II) and Cu (II) adjusted better to the Langmuir model (37). The experimental adsorption data were fitted to the Langmuir adsorption model with  $R^2=0.998$  for both sawdust and activated sawdust (24). The Langmuir and Freundlich isotherm models were applied for modeling of the adsorption equilibrium data, and finally the Langmuir isotherm model described the equilibrium data with  $R^2=0.9997$  (13). Following equilibrium sorption data from the Langmuir isotherm means that the adsorption occurs at specific homogeneous sites within the adsorbent and is based on the monolayer adsorption of ions on surface of sites (26, 31). The equilibrium adsorption data fits the linear Langmuir and Freundlich isotherms according to Yu *et al.*'s study (32). Semerjian found that the equilibrium adsorption data were best fitted with the Freundlich isotherm ( $R^2=0.960$ ) (41). This isotherm describes the heterogeneous surface energies by multilayer adsorption (26).

### **The effect of temperature on removal efficiency**

Depending on whether adsorption process is endothermic or exothermic, temperature will be effective in increasing or decreasing of this process (6). In Karthikeyan *et al.*'s study, enthalpy was obtained  $\Delta H=35.144$  kJ/mol that the positive value indicates that the adsorption process is endothermic (26). In Meena *et al.*'s study, the adsorption of metal ions has been increased with an increase in temperature from 20 to 60 C that indicates an endothermic process, and removal efficiency improved. The increase in adsorption with temperature may be attributed to either change in pore size of the adsorbent causing intraparticle diffusion within the pores or increase in the chemical affinity of the metal cations to the adsorbent surface(6). The negative value of  $\Delta H$  shows the exothermic nature of adsorbtion, so, with decreasing temperature, removal efficiency has increased (42). With increase in temperature from 293 to 323 °K, the adsorption capacity increased from



20.78 to 63.99 mg/g for the initial concentration of 200 mg/L at pH 2.0. Similar trends are observed for the other concentrations. This indicates that the adsorption reaction is endothermic. The enhancement in the adsorption capacity may be due to the chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of ions into the pores of the adsorbent at higher temperatures (26). In another research, when the temperature is increased from 30 to 80°C, capacity increased from 26.03 to 43.42 mg/g for Ni and decreased from 11.66 to 2.67 mg/g for Zn. The percentage removal increased for Ni and decreased for Zn. Therefore, the metal removal process is endothermic for Ni and exothermic for Zn. The increase in adsorption may be due to the increase in active surface centers available for adsorption with temperature. This leads to an enhanced rate of intraparticle diffusion of Ni ions (31). The negative value of  $\Delta G^0$  (changes of Gibbs free energy) confirms the spontaneous nature of the biosorption (43). When the reaction is endothermic, it means by increasing temperature, spontaneity of the reaction can increase and as a result, the metal adsorption capacity and  $\Delta S$  (entropy changes) value are also increased (1). It has been reported that negative value of  $\Delta H$  (enthalpy changes) and  $\Delta G$  (Gibbs free energy changes) shows the exothermic and spontaneous nature of reaction (44).

#### Adsorption kinetics

The kinetics of adsorption describes the rate of uptake of chromium ions onto the activated carbon and this rate controls the equilibrium time (26). Among 39 experiments, 24 experiments had determined adsorption kinetics, that pseudo second-order with 75% and pseudo first-order with 25% frequency were accorded with data. In Semerjian's study, the kinetics of cadmium adsorption was very well described by the pseudo-second-order kinetic model ( $R^2 > 0.999$ ) (41). The adsorption

kinetics tested with pseudo-first-order and pseudo-second-order models and finally followed from pseudo-second-order model (2) that means the initial concentration of heavy metal correlates directly with the square of rate, whereas in the first-order kinetics is this relationship directly. Various mechanisms control the kinetics in the sorption phenomena. Four major rate-limiting steps are generally cited: (1) mass transfer of solute from solution to the boundary film, (2) mass transfer of metal ions from boundary film to surface, (3) sorption of ions onto sites and (4) internal diffusion of solute. The third step is assumed to be very rapid and non-limiting in this kinetic analysis. The first and the second steps are external mass transfer resistance steps, depending on various parameters such as agitation and homogeneity of solution. The fourth one is an intraparticle diffusion resistance step (45).

#### Conclusion

Our main results from the present study are as follows:

- 1) Maximum of removal efficiency was occurred at acidic pH;
- 2) Effect of increasing and decreasing temperature on adsorption efficiency was determined with reaction enthalpy;
- 3) By increasing the adsorbent dose and initial concentration of heavy metal, the removal of heavy metals was decreased;
- 4) With increasing time to reach equilibrium time, the removal efficiency was increased.

According to the results, it can be concluded that sawdust can be used as a low cost, natural, and abundant availability adsorbent with the same efficiency of synthetic adsorbents for removal of heavy metals ions from aqueous solution.

#### Conflict of Interest:

The authors declare no conflict of interest.

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