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# Aqueous Cadmium Removal by Adsorption on Barley Hull and Barley Hull Ash

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Adsorbents prepared from barley hull and barley hull ash, an agricultural waste product, were used to remove cadmium from an aqueous solution in batch mode as a function of appropriate equilibrium time, amount of adsorbent, concentration of adsorbate, pH and particle size. Studies showed that pH of aqueous solutions affected cadmium removal as a result of removal efficiency increased with increasing solution pH. The maximum adsorption was about 95.8 and 99.2 % for barley hull and barley hull ash, respectively, at pH 9, contact time 180 min and initial concentration of 30 mg $L^{-1}$. Desorption of cadmium was 8 % at pH 9. The cadmium sorption obeyed both the Langmuir and Fraundlich isotherms. The sorption kinetics are well described by the pseudo-second-order kinetic model. The studies showed barley hull ash was more favourable than barley hull in removing cadmium and thus was a better adsorbent as low-cost alternatives in wastewater treatment for cadmium removal.

**Key Words: Barley hull, Barley hull ash, Cadmium, Adsorption, Desorption.**

## INTRODUCTION

The contamination of water by toxic heavy metals through the discharge of industrial, mining and agricultural wastewaters is a worldwide environmental problem[1,2]. Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain[3,4]. Cadmium is a highly toxic element affecting the environment. Excessive human intake of Cd leads to damage of kidney and renal system, skeletal deformation (Itai-itai), cardiovascular diseases and hypertension. Severe gastrointestinal irritation, muscular pain, anemia, teeth discoloration, loss of smell and possible necrotic changes in the liver and kidney can also occur. Cadmium is also known carcinogen[5]. The treatment of cadmium contaminated water is similar to that of many metal contaminated effluents. The main techniques, which have been utilized to reduce the heavy metal ion content of effluents, include chemical precipitation, coagulation, lime precipitation, solvent extraction, electrolytic processes, membrane separation, ion-exchange and adsorption[1,3,6].

In the last few years, adsorption has been shown to be an economically feasible alternative method for removing trace metal from wastewater and water supplies[7-9]. Activated carbon has been the most used adsorbent; nevertheless it is relatively expensive[7,10]. Cost is an important parameter for comparing the adsorbent materials. Therefore, numerous approaches have been studied for the development of low-cost adsorbents[3]. Bottom ash, brick-kiln ash, fly ash, peat, soil, rice husk, wood, saw dust, bagasse and carbonized bark are some new adsorbent used for organic pollutants[9,11]. In the search for new and low cost agricultural wastes as source material for widely uses, barley hull and barley straw are an agricultural waste produced as by-product of the barley milling industry[9,12]. The utilization of this source of biomass would solve both a disposal problem and also access to cheaper material for adsorption in water pollutants control system[13]. Chemical composition (w/w) of raw barley hull consists of cellulose (37.5 %), hemicelluloses (36.1 %), lignin (15.5 %), ash (4.8 %) and wax (2.5 %)[14]. The availability of specific functional groups such as hydroxyl existing in the cellulose, hemicelluloses as well as lignin structure suggests a potential of using barley hull as an adsorbent material[15]. The barley hull ash has more than 90 wt % of silica with high porosity and large surface area, because it retains the skeleton of cellular structure. These properties of the barley hull ash can are used to synthesize siliceous raw materials such as clay materials[16].

The aim of this study is to explore the possibility using barley hull and barley hull ash for removing cadmium from aqueous solution. The influences of various factors, such as contact time, adsorbent dose, adsorbent size, initial pH and initial pollutant concentrations on the sorption capacity were also studied. The Freundlich and Langmuir models were used to analyze the adsorption equilibrium.

## EXPERIMENTAL

Stock solution of cadmium (1000 mg $L^{-1}$) was prepared by dissolving cadmium nitrate in distilled water. The concentration range of cadmium prepared from stock solution varied between 10-50 mg $L^{-1}$ for both adsorbents. Before mixing the adsorbent, the pH of each solution was adjusted to the required value with diluted and concentrated $H_2SO_4$ and NaOH solution, respectively. All the chemicals used were of analytical reagent grade and were obtained from Merck.

**Preparation of adsorbent:** The barley hull used was obtained from the west part of Iran. The barley hull were crushed and sieved with 40, 50, 60, 80 and 100 mesh sieve. Then, the hulls were thoroughly washed distilled water to remove all dirt and were dried at 100 ºC till constant weight. The dried straws were stored in desiccator until used. The barley hull ash obtained from burning of barley hull in electrical oven at 500 ºC for 3 h. The barley hull ash was sieved with a 120-mesh siever and stored in a desiccator until used.

**Analysis of cadmium:** The determination of residual cadmium was performed by atomic absorption spectrometry using a PG 990-flame atomic absorption spectrophotometer (PG Instrumentation, UK) at wave lengths 228.8 nm using an acetylene-air flame according to standard methods[17].

**Adsorption studies:** Adorption studies were conducted in a routine manner by the batch technique. Each cadmium solution was placed in 1000 mL beaker and a known amount of adsorbents (1-5 g) were added to each beaker. The beakers were agitated on a shaker at 120 rpm constant shaking rate for 6 h to ensure equilibrium was reached. Then, samples analyzed for the remaining cadmium. Desorption study was carried out by taking 2 g of cadmium loaded adsorbent and 1000 mL of distilled water and agitating for 24 h at 120 rpm. pH of the desorbing medium (water) was adjusted to fix pH value at 7 and per cent desorption was determined. Finally the suitability of the Freundlich and Langmuir adsorption model to the equilibrium data were investigated for cadmium-sorbent system. All the experiments were carried out in duplicate and mean values are presented.

## RESULTS AND DISCUSSION

The adsorption of cadmium in aqueous solution on barley hull and its ash were examined by optimizing various physicochemical parameters such as pH, contact time, desorption, amount of adsorbent, adsorbent size and adsorbate.

**Effect of initial pH:** It is known that the sorption of heavy metal ions by adsorbents depends on the pH of the solution. This study was carried in the pH range 2-10 as the metal solutions were precipitated above pH 10. Fig. 1 shows the percentage adsorption of cadmium on barley hull and its ash increased as pH of the solution was increased and reach to maximum value at pH 9. Adsorption of metal cation on adsorbent depends upon the nature of adsorbent surface and species distribution of the metal cation[12]. At pH 2 the sorption was about 28 % on barley hull. Increasing, the pH by 2 units, the uptake increased to about 67 %. This sharp increase in the sorption efficiency could be explained in two ways. Firstly, at low pH, protons compete with metal ion for sorption sites on the adsorbent surface. This phenomenon could be confirmed by the observation of sharp increase in the final solution pH of those having low initial pH values. Secondly, for each hydrolyzable metal ion, there was a critical pH range (often 2 units wide) where the metal uptake efficiency increased from a very low level to maximum value[3]. This pH value is commonly called as the adsorption edge. Decreasing trend in uptake was observed above pH 9 due to formation of soluble hydroxyl complexes.

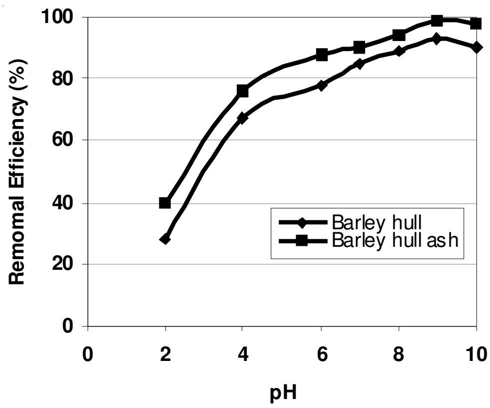


Fig. 1. Effect of pH on the removal of cadmium by barley hull and barley hull ash (adsorbent dosage = 5 g $L^{-1}$, cadmium concentration = 30 mg $L^{-1}$)

**Effect of contact time:** The adsorption of cadmium increased with increasing contact time and became almost constant after 55 min for barley hull and 0.5 h for its ash (Fig. 2). These results also indicate that the sorption process can be considered very fast because of the largest amount of cadmium attached to the adsorbent within the first 0.5 h of adsorption. Similar results reported by Ajmal *et al.*[1] and Kumar and Bandyopadhyay[3] for adsorption of cadmium by rice husk.

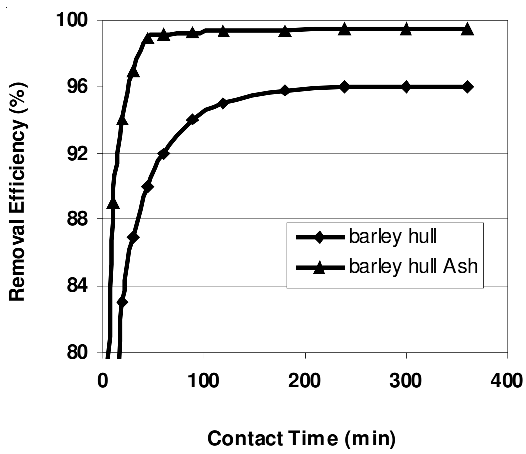


Fig. 2. Effect of contact time on the removal of cadmium by barley hull and barley hull ash (adsorbent dosage = 5 g $L^{-1}$, cadmium concentration = 30 mg $L^{-1}$)

**Effect of adsorbent amount:** The amount of adsorbent on the efficiency of adsorption was also studied. Fig. 3 shows the removal of cadmium by barley hull and its ash at the solution pH of 7. The percentage adsorption increased from 55-92 % for barley hull and from 72.0-99.2 % for barley hull ash when adsorbents doses were increased from 1-5 g $L^{-1}$ for both adsorbents, but at the same time adsorption density decreased from 16.5-5.52 mg $g^{-1}$ for barley hull and from 21.6-5.95 mg $g^{-1}$ for its ash. Similar results reported by other Namasivayam and Ranganathan[18]. It is evident that for the quantitative removal of different value of cadmium in 100 mL a high dosage of barley hull is required. The data clearly shows that the barley hull ash is more effective than barley hull for removal of cadmium.

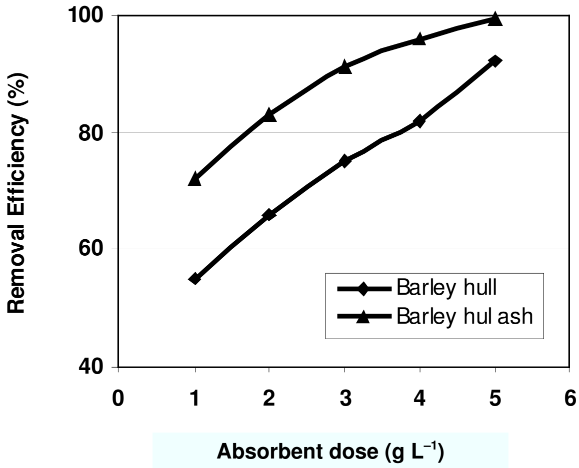


Fig. 3. Effect of adsorbent dose on the removal of cadmium by barley hull and barley hull ash (pH = 9, cadmium concentration = 30 mg $L^{-1}$)

**Effect of initial cadmium concentration:** The equilibrium sorption capacities of the adsorbents obtained from experimental data at different initial cadmium concentration are presented in Fig. 4. As seen from results, the sorption capacities of the adsorbents increased with increasing cadmium concentration while the adsorption yields of cadmium showed the opposite trend. When the initial cadmium concentration was increase from 10-50 mg $L^{-1}$ on barley hull and barley hull ash, the loading capacity increased from 1.98-8.00 mg/g of barley hull and from 1.99-9.50 mg/g of barley hull ash. Increasing the mass transfer driving force and therefore the rate at which cadmium molecules pass from the bulk solution to the particle surface. On a relative basis, however, the percentage adsorption of cadmium decreases (Fig. 4) as the initial cadmium concentration increases. The equilibrium uptake and adsorption yield were highest for the barley hull ash, which was expected, because of the greater specific surface area and the microporous structure of barley hull ash compared with barley hull.

**Effect of particle size:** The adsorption capacity of barley hull very much depends on the surface activities. In other words, specific surface area available for solute surface interaction, which is accessible to the solute. Adsorption being a surface phenomenon, the smaller adsorption sizes will offer comparatively larger surface areas and higher adsorption will occur at equilibrium[19]. It is expected that adsorption capacity will be increased with a larger surface area. In other words,

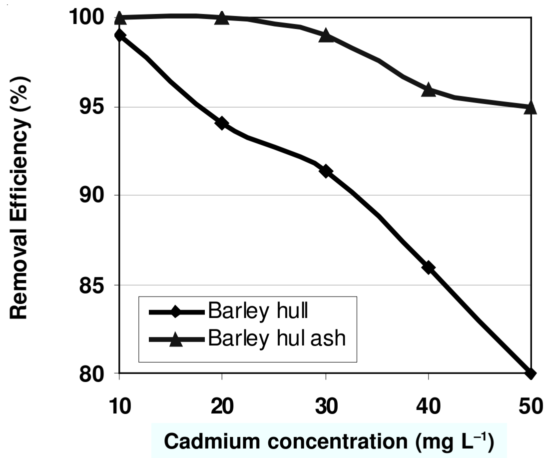


Fig. 4. Effect of cadmium concentration on the removal of cadmium by barley hull and barley hull (adsorbent dosage = 5 mg $L^{-1}$, pH = 9)

smaller particle size increases the adsorption capacity. For this reason the batch adsorption experiments were carried out using the six particle size at fixed pH (9), adsorbent dose (5 g), contact time (3 h). The selected particle mesh sizes were 40, 50, 60, 80 and 100. The percentage adsorption of cadmium was found to be 92, 91.5, 92.4, 93.5 and 95 using the above mentioned size, 40 was selected for adsorption studies due to the sufficient adsorption capacity and easiness of preparation (Fig. 5).

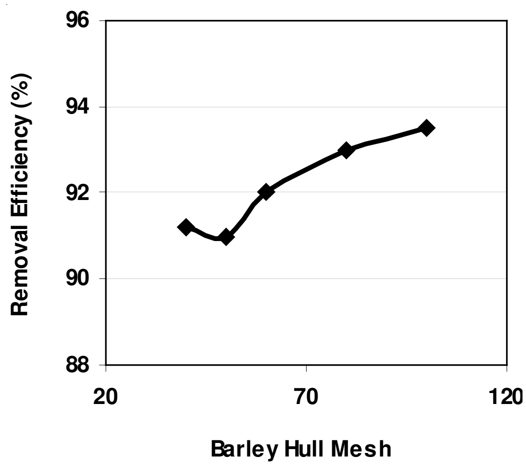


Fig. 5. Effect of barley hull size on the removal of cadmium (cadmium concentration = 30 mg $L^{-1}$, rice husk dose = 5 g $L^{-1}$)

**Adsorption isotherms:** Experimental isotherm are useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application, for selection of the most appropriate adsorbent and for preliminary determination of adsorbent dosage requirements. Moreover, the isotherm plays an important role in the predictive modeling procedures for analysis and design of sorption systems. The Langmuir and Freundlich isotherms are most frequently used to represent the data of sorption from solution. In order to establish the maximum sorption capacity, the Langmuir equation of the following form was applied to the sorption equilibria at different adsorbent doses.

Two models, Langmuir and Frendlich equations, were used to determine adsorption of cadmium onto barley hull and its ash. Isotherm studies were then carried out as described in earlier study[8]. The related parameters of Langmuir and Frendlich models are summarized in Table-1.

TABLE-1
PARAMETERS OF FREUNDLICH AND LANGMUIR ISOTHERM MODELS

| | Freundlich constants | | | Langmuir constants | | |
|---|---|---|---|---|---|---|
| | K | 1/n | $R^2$ | Qº | b | $R^2$ |
| Barley hull | 3.88 | 0.3083 | 0.99 | 6.06 | 4.78 | 0.92 |
| Barley hull ash | 7.5 | 0.2319 | 0.92 | 8.4 | 33.06 | 0.96 |

The adsorption capacity (Qº) and energy of adsorption (b) were determined from the slope and intercept of the Langmuir plot and found to be (Qº) 6.06 and 8.4 and (b) 4.78 and 33.06, onto barley hull and its ash, respectively.

The Frendlich isotherm was also used to explain observed phenomena. K and n values were calculated from the intercept and slope of the plot and found to be (K) 3.88 and 7.51 and (1/n) 0.3083 and 0.2319 onto barley hull and its ash, respectively.

The Freundlich isotherm obeyed better than the Langmuir isotherm as is evident from the values of regression coefficients (Table-1). Similar results were reported by Ajmal *et al.*[1] for adsorption of cadmium on rice husk from wastewater.

**Desorption studies:** Desorption studies help recycling of the adsorbent and recovery of metal. The batch desorption experiment were carried out using distilled water at fix pH value, adsorbent dose (2 g) and contact time (24 h). The results showed that the desorption of cadmium by batch process was 8 %. Other experiments showed that the per cent desorption of cadmium increased with decrease in pH value. At acidic condi-tions, $H^+$ ions protonate the adsorbent surface leading to the desorption of the positively charged metal ion species[18].

## Conclusion

In this study, the ability of barley hull and its ash to adsorb cadmium from aqueous solution has been explored. The extent of removal depended on concentration of the adsorbate, pH, contact time, adsorbent size and adsorbent amount. Cadmium adsorption capacity was strongly dependent on the pH of the solution. The sorption capacity was increased with an increase in the pH and an increase in the initial cadmium concentration. Freundlich and Langmuir adsorption models expressed the sorption phenomena of cadmium to the barley hull and its ash. Consequently, linear regression of the experimental data showed that the Freundlich equation best represented cadmium adsorption data. The model parameters would be useful for fabrication and designing of wastewater treatment plants. On the bases of this study, it may be concluded that barley hull and its ash especially, may be used as low cost, natural and abundant sources for the removal of cadmium. Moreover, barley hull ash has adsorption capacity more than barley hull for cadmium removal.

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