# Removal of Cadmium from Aqueous Solutions by Hazel Nut Shell

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**Abstract:** The adsorption behavior of hazelnut shell and its ash for cadmium ions from aqueous solution has been investigated as a function of appropriate equilibrium time, amount of adsorbent, concentration of adsorbate, pH and particle size using a batch system. Experiments were conducted by use of jar test apparatus. Studies showed that pH of aqueous solution affected cadmium adsorption as a result of removal efficiency increased with increasing solution pH but after pH about 6 the removal efficiency decreased. The maximum adsorption were about 98.2 and 99.1% for hazelnut shell and its ash, respectively, at pH 6, contact time 180 minutes and initial concentration of 30 mgL$^{-1}$. Desorption of cadmium was 12% at pH 6 the cadmium sorption obeyed both the Langmuir and Freundlich isotherms. The studies showed that hazelnut shell ash was more favorable than hazelnut shell in removing cadmium and thus, was a better adsorbent.

**Key words:** Cadmium removal · Hazelnut shell · Ash · Adsorption · Aqueous system

## INTRODUCTION

Trace heavy metals play an important role as micronutrients in organisms. However, many metals have toxic effects in high concentration [1, 2]. Cadmium has various applications in a variety of industrial processes and operations and is released through natural processes such as volcanic activities [3, 4].

It directly meets water bodies through the effluent of industries causing a marked increase in its concentration. The major sources of cadmium release into environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes [5, 6].

A number of treatment methods for the removal of metal ions from aqueous solutions have been reported are reduction, ion exchange, electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reveres osmosis, chemical precipitation, ultra filtration and adsorption [7, 8]. Most of these methods suffer from some drawbacks such as high capital and operational costs. Disposal of the residual metal sludge causes problem for small-scale Industries. Also these methods are inadequate when the permissible concentrations of the metal ions are low [9, 10].

The objective of the present study was to search for low-cost locally available biosorbent with respect to their efficiency in the removal of cadmium from simulated contaminated samples. Since the performance of any biosorbent depends on biomass characteristics and the microenvironment of target metal–solution, the effects of different physical-chemical parameters on the adsorption process by Hazelnut shell and its ash, were investigated.

Cadmium has been recognized as one of toxic metals. Toxic effects of cadmium on humans include both chronic and acute disorders like testicular atrophy, hypertension, damage to kidneys and bones, anemia, itai-itai, etc. [11-15].

Cadmium has an extremely long biological half-life (>20 years) and it is listed by the US-EPA as one of the 126 priority contaminants and as a known carcinogen by the International Agency For Research on Cancer [16].

Many of researches are carried out on the development of technology for the removal of cadmium ions from the effluent before discharging into water system. The use of platanus oriental leaves and other agricultural fibers have good efficiencies in adsorption of heavy metals [17, 18]. Other process such as electrocoagulation has also been used for the removal of heavy metals [19].

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## MATERIALS AND METHODS

**Preparation of Sorbent:** The raw material for this study was obtained from the city of Qazvin in Iran. The Hazelnut shell were crushed and sieved with 40, 50, 60, 80 and 120 mesh sieve. Then, the hazelnut shells were thoroughly washed with distilled water to remove all dirt and then were dried at 100°C to have constant weight. The dried hazelnut shells were stored in desiccator until used. The hazelnut shell ash obtained from burning of hazelnut shell in electrical oven at 600°C for 3 hours.

**Chemicals:** Stock solution of cadmium (1000 mgL$^{-1}$) was prepared by dissolving cadmium nitrate in distilled water. The concentration range of cadmium prepared from stock solution varied between 10 to 100 mgL$^{-1}$ for both hazelnut shell and its ash. Before mixing the adsorbent, the pH of each last solution was adjusted to the required value by the addition of 0.1 N NaOH or 0.1 N H$_2$SO$_4$.

**Adsorption Studies:** Batch mode adsorption studies were carried out to determine the adsorption of cadmium. Each cadmium solution was placed in 1000 ml beaker and a known amount of adsorbents (0.5 to 10g) were added to each beaker. The beakers were agitated on jar test equipment at a 120 rpm constant mixing rate for 3h to ensure that equilibrium was reached. Desorption study was carried out by taking 2gr of cadmium loaded absorbent and 1000 ml of distilled water and agitating for 24h at 120 rpm. pH of the desorbing medium (water) was adjusted to fix pH value (6) and percent adsorption was determined. At the end 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.

**Analysis of Cadmium:** The residual cadmium was analyzed through atomic absorption spectrometry using an ALPH-4 - Flame atomic absorption spectrophotometer at wave lengths 228.8 using an acetylene-air flame according to standard methods [20].

## RESULTS AND DISCUSSION

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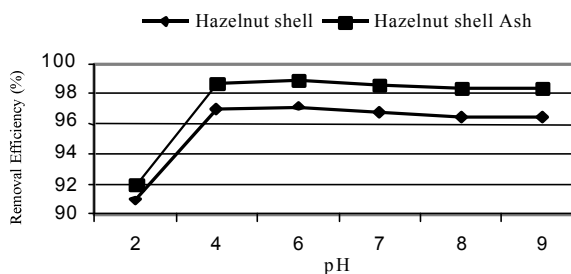


Fig. 1: Effect of pH on the removal of Cadmium by hazelnut shell and hazelnut shell ash (adsorbent dosage = 2gL$^{-1}$, Cadmium concentration = 20 mgL$^{-1}$)
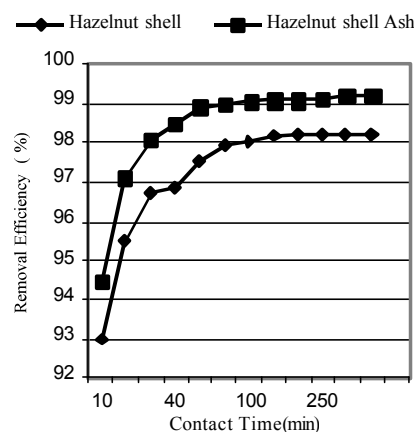


Fig. 2: Effect of contact time on the removal of cadmium by hazelnut shell and hazelnut shell ash (Adsorbent dosage 2gL$^{-1}$, Cadmium concentration = 30 mg L$^{-1}$

**Effect of Initial pH:** Metal sorption is greatly influenced by pH as different metals not only show different pH optima but that also depends on the kind of biomass [21].

Adsorption of cadmium at pH 2 was very low. One of the reasons for this poor adsorption may be due to competition for the negatively charged binding sites of the Hazelnut shell and its ash between Cd ions and H$^+$ or H$_3$O$^+$ ions present in the medium at this low pH.

As expected, sorption had been found to enhance with increase in pH to reach optimum at pH 5-6 (Fig. 1).

Decrease in sorption noted with further increase in pH may be attributed to low solubility of cadmium at high pH. Moreover, speciation of cadmium ions shows that beyond pH 7 it exist as [Cd (OH)$_3$]$^-$ or [Cd(OH)$_4$]$^{-2}$ causing repulsion with the negatively charged binding sites of the adsorbent [22]. The present findings corroborated the earlier report by saeed and Iqbal [23] for bioremoval of cadmium from aqueous solution by black gram husk.
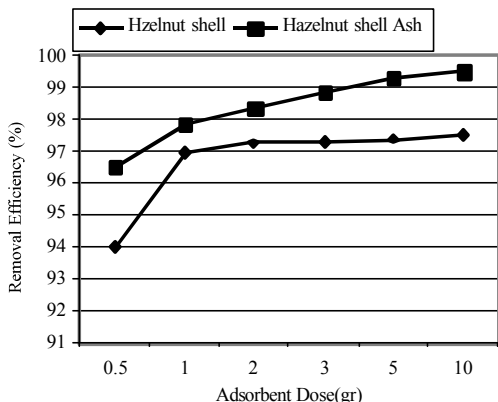
Fig. 3: Effect of adsorbent dose on the removal of cadmium by hazelnut shell and hazelnut shell ash
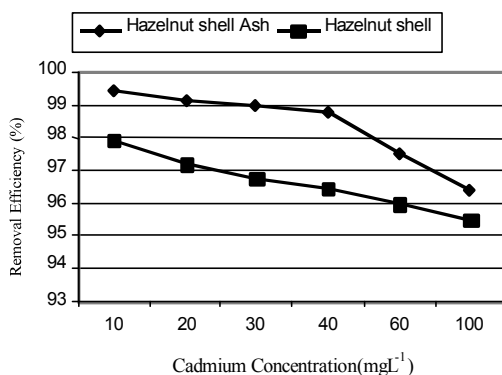


Fig. 4: Effect of cadmium concentration on the removal of cadmium by hazelnut shell and hazelnut shell ash (Adsorbent dosage = 2 $gL^{-1}$ pH=6)

**Effect of Contact Time:** The adsorption of cadmium increased with increasing contact time and become almost constant after 75min for hazelnut shell and 60 min for its ash (Fig. 2).

These results also indicate that the extent of adsorption increased rapidly in the initial stages but slowed in the later stages until the attainment of equilibrium. Similar results were reported by Raji *et al.* [24] and Huang *et al.* [25].

**Effect of Adsorbent Amount:** The removal of cadmium by hazelnut shell and its ash at the solution pH 6 shows in Fig. 3. The percentage adsorption increased from 94 to 97.5% for hazelnut shell and from 96.5 to 99.5% for hazelnut shell ash when adsorbent dose were increased from 0.5 to 10 $gL^{-1}$ for both sorbates, but at the same time adsorption density decreased from 40.2 to 2.5 mg $g^{-1}$ for hazelnut shell and from 42.1 to 2.8 mg $g^{-1}$ for hazelnut shell ash. Similar results reported by Marshall and Johns [26].
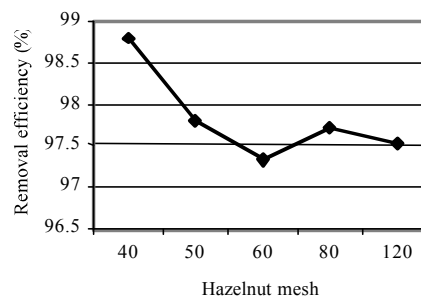


Fig. 5: Effect of hazelnut shell size on the removal of cadmium (Cadmium concentration = 20 $mgL^{-1}$, hazelnut shell dose = 2 $gL^{-1}$)

**Effect of Initial Concentration:** The equilibrium sorption capacities of the sorbents obtained from experimental data at different initial cadmium concentration are showed in Fig. 4. As seen from the results, the sorption capacities of the sorbent increased with increasing cadmium concentration while the adsorption yields of cadmium showed the opposite trend. Increasing the mass transfer driving force and therefore the rate at which cadmium ions pass from the bulk solution to the particle surface. This would results in higher adsorption [27, 28, 29].

**Effect of Particle Size:** The batch adsorption experiments were carried out using the six particle size at fixed pH (6), adsorbent dose (2gr) and contact time (3 h). The selected particle mesh sizes were 40, 50, 60, 80 and 120. The percentage adsorption of cadmium was found to be 98.8, 97.8, 97.3, 97.7 and 97.5. Using the above mentioned size, 40 was selected for adsorption studies due to the sufficient adsorption capacity and easiness of preparation. The results are given in Fig. 5.

**Desorption Studies:** Desorption studies help recycling of the adsorbent and recovery of metals. The batch desorption study were carried out using distilled water at fix pH value, Adsorbent dose (2gr) and contact time (24h). The results showed that the desorption of cadmium by batch process was 12%. Almost similar results were reported by NamaSivayam *et al.* [27].

**Adsorption Isotherms:** Two models, Langmuir and Freundlich equations, were used to determine adsorption of cadmium on to hazelnut shell and its ash. Isotherm studies were then carried out as described in our earlier paper [29]. The related parameters of Langmuir and freundlich models are summarized in Table 1.

The adsorption capacity (Q°) and energy of adsorption (b) were determined from the slope and intercept of the langmuire plot and found to be (Q°) 0.039

Table 1: Parameters of Freundlich and Langmuir Isotherm models

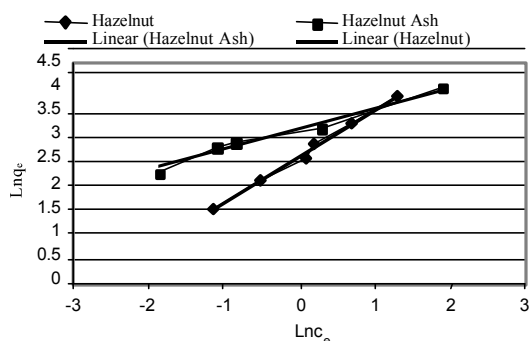| | Freundlich constants | | | Langmuir constants | | |
|---|---|---|---|---|---|---|
| | K | 1/n | $R^2$ | $Q°$ | b | $R^2$ |
| Hazelnut shell | 0.96 | 0.39 | 0.993 | 0.039 | 0.0072 | 0.963 |
| Hazelnut shell ash | 0.44 | 0.316 | 0.985 | 0.0041 | 0.047 | 0.985 |



Fig. 6: The linearized Freundlich adsorption isotherm for cadmium by hazelnut shell and hazelnut shell ash
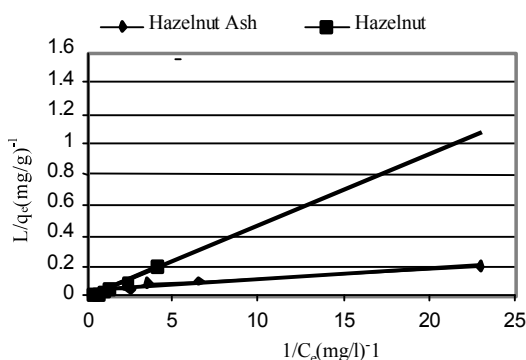


Fig. 7: The linearized Langmuir adsorption for cadmium by hazelnut shell and hazelnut shell ash

and 0.0041 and (b) 0.0072 and 0.047 onto hazelnut shell and its ash respectively.

The Freundlich 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) 0.96 and 0.44 and (1/n) 0.39 and 0.316 onto hazelnut shell and its ash respectively.

The Freundlich isotherm is obeyed better than the Langmuir isotherm as is evident from the values of regression coefficient in Table 1. The results are given in Fig. 6 and 7. Similar results were reported by Ajmal *et al*. [30].

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