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Thermodynamics of removal of cadmium by adsorption on Barley husk biomass

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ABSTRACT

The adsorption ability of barley husk biomass for removing Cd (II) has been studied using cold vapour atomic absorption spectrometry. A dose of 3 g/L of dried biomass in a solution with an initial pH of 7, an initial Cd(II) concentration of 10 mg/L and a contact time of 90 min resulted in the maximum Cd(II) removal efficiency (95.9%). The effect of temperature on cadmium sorption on barley husk was thoroughly examined. Consistent with an exothermic reaction, an increase in the temperature resulted in decreasing Cd (II) adsorption rate. Thermodynamic parameters (i.e., change in the free energy (ΔG^o), the enthalpy (ΔH^o), and the entropy (ΔS^o)) were also evaluated. The overall adsorption process was exothermic and spontaneous in nature. These results suggest that barley husk could be employed as an efficient adsorbent for the removal of cadmium from contaminated water sources.

Keywords: Cadmium, Adsorption, Barley husk, Thermodynamics

INTRODUCTION

Recovery of pollutants from waste water and industrial waste has become a very important environmental issue[1,2]. The presence of heavy metals contaminated in aqueous streams, arising from the discharge of untreated metal containing effluent into water bodies[3,4]. They are non-degradable in the environment and can be harmful to a variety of living species[5,6]. Besides the toxic and harmful effects to organisms living in water, heavy metals also accumulate throughout the food chain and may affect human beings[7,8]. For that reason, the removal of these metals from waters and wastewaters is important in terms of protection of public health and environment[9,10].

Cadmium is one of the most toxic heavy metals, it has been reported to cause renal dysfunction, hypertension, lung insufficiency, bone lesions, cancer, etc[11,12]. The drinking water guideline value recommended for this element by the WHO and American Water Works Association (AWWA) is 0.005 mg/L[13]. The principal industrial sources of Cd in the environment are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes[14-16].

Treatment processes for metal contaminated waste streams include chemical precipitation, membrane filtration, ion exchange, carbon adsorption, and co-precipitation/adsorption[17,18]. Among these, adsorption process has been found as one of the most promising technologies in water pollution control in terms of cost, simplicity of design and operation[19,20]. Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications throughout the world and has been successfully utilized for the removal of diverse types of pollutants including metal ions[21,22]. However, the high capital and regeneration cost of the activated carbon limits its large-scale applications for the removal of metals and other aquatic pollutants, which have encouraged researchers to look for low-cost alternative[23,24].

The barley husk is one agricultural residue which can be used as low-cost adsorbent[25]. Recently, the residues of barley husk are going to be greater and more available due to increase the tendency to consume the vegetable oils in Iran and the entire world[26, 27]. The residues of barley husk have been used as adsorbent in several studies and have been indicated the acceptable results to remove the pollutants[28, 29]. The objective of the present work is to investigate the biosorption potential of barley husk biomass in the removal of Cd(II) ions from aqueous solution. Optimum biosorption conditions were determined as a function of initial Cd(II) concentration, contact time, and temperature.

MATERIALS AND METHODS

In this study, the Barley husk was used as low cost natural or agricultural wastes for Cd (II) removal from aqueous solutions. The stalks of Barley husk (C) were collected from research farm of Tabriz agricultural school. The stalks were washed several times with water to remove the contaminant, dried in the oven at 105℃ for 5 h. The biomass were then treated with 0.5 M H_2SO_4 for 3 h followed by the washing with distilled water and then was oven dried at 105℃ for 5 h. After drying, adsorbent were sieved to obtain particle size of 18 mesh prior to being used for adsorption studies.

Chemicals and reagents

All of the chemicals and reagents were at least of analytical grade and used without further purifications. The Cd (II) ion stock solutions with a concentration of 1000 mg/L were prepared

from their corresponding nitrate salts. The metal ion solutions were subsequently diluted with deionized water to obtain desired concentration ranging from 10 to 100 mg/L. All the tested plastic bottles and glasswares were presoaked in a 20% HNO_3 solution for 3 days, rinsed with deionized water and oven-dried before each experiments.

Batch adsorption experiments

Batch adsorption experiments were carried out by agitating 0.3 g of the adsorbent with 100 ml aqueous solution of cadmium at temperature 30 ℃ in different polythene bottles on a shaking thermostat at 180 rpm. After predetermined time intervals, the adsorbent was separated from solutions by a 0.45 μm cellulose acetate membrane without centrifugation. The filtrate was then analyzed by an atomic absorption spectrophotometer (Shimadzu AA 6300) that is equipped with both flare combustion and graphite furnace spectrophotometer, which were employed respectively according to different concentrations. Influence of pH on adsorption was also examined by adjusting initial solution pH using 0.1 M nitric acid and sodium hydroxide solutions.

RESULTS AND DISCUSSION

The contact time between adsorbate and adsorbent is the most important design parameter that affects the performance of adsorption processes. The adsorption capacity and %removal of Barley husk versus the contact time is shown in Fig. 1 and 2. The figure revealed that the adsorption capacity increased with the contact time up to 90 min when the maximum adsorption is reached. Therefore the optimum contact time was chosen as 90 min.

Figures 1 and 2 show the effect of Cd (II) concentration on the adsorption of Cd (II) by Barley husk. The data shows that the Cd (II) uptake increases and the percentage adsorption of Cd (II) decreases with increase in metal ion concentration. This increase (3.19- 22.98 mg/g) is a result of increase in the driving force, i.e. concentration gradient. However, the percentage adsorptions of Cd(II) on Barley husk were decreased from 95.9 to 68.96%. Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution[30,31]. The percentage adsorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of Cd (II) displays an opposite trend. At lower concentrations, all Cd (II) present in solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher Cd(II) concentrations[32,33]. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. As a result, the purification yield can be increased by diluting the wastewaters containing high Cd(II) concentrations[34,35].

Effect of temperature on the removal

Temperature is an important parameter and has pronounced effect on adsorption. During the present investigations the removal of cadmium decreased from 95.9.% to 69.4% by increasing the temperature from 283 to 328 K (Fig. 1) at an initial cadmium concentration of 10 mg/L. The higher ionic strength helps eliminating the effects of change in concentration during the process of removal. The experiments were conducted at 6.5 pH and agitation speed was maintained at 180 rpm. It is clear that like most adsorption processes, removal of cadmium is also an exothermic reaction. It is also clear from this figure that equilibrium was established in 90 min. This variation in removal of cadmium seems due to the enhancement of relative escaping tendencies of the metal ions from aqueous phase to the bulk and consequent reduction in the boundary layer thickness[36,37]. The decrease in the removal at increasing temperatures can also be attributed to the increased solubility of metal at relatively higher temperatures[38,39].

The other thermodynamic parameters of concern are change in standard free energy, ΔG◦, change in standard enthalpy, ΔH◦, and the change in standard entropy, ΔS◦. Values of these parameters were calculated at 283, 298, 313, and 328 ◦C respectively. For the present investigations, values of these parameters were determined using following standard equations[40-42]:

$\Delta G^\circ = -RT \ln K$
$\Delta H^\circ = R(T_2T_1/(T_2\text{-}T_1)) \ln K_2/K_1$
$\Delta S^\circ = \Delta H^\circ - \Delta G^\circ/T$

where 'R' is gas constant (8.314 J $mol^{-1}K^{-1}$), K, K_1, and K_2 are equilibrium constants at temperatures T, T_1, and T_2, respectively. 'K' is related to Langmuir's constant. The values of ΔG◦, ΔH◦ and ΔS◦ calculated for the present studies have been given in Table 1 and shows that the values of all the parameters are negative and further confirm exothermic nature of the process of cadmium removal. Under different temperatures (283, 298, and 313 and 328 K), the negative ΔG◦ values of 6.975, 7.144, 7.396 and 7.672 $Jmol^{-1}$ indicated the spontaneous nature of Cd (II) adsorption by barley husk. The magnitude of ΔG◦ increased along with increasing temperature, implying an increased degree of spontaneity at a higher temperature for its advantage of the chelating interaction between amine groups and mercury. From the van't Hoff plot (ln K versus 1/T; plot not shown), the negative ΔH◦ values of (3.244 mol^{-1}) confirmed the exothermic nature adsorption, while the negative values of ΔS◦ (19.24 mJ mol^{-1} K^{-1}) revealed the decreased randomness (orderliness) at the solid/solution interface.

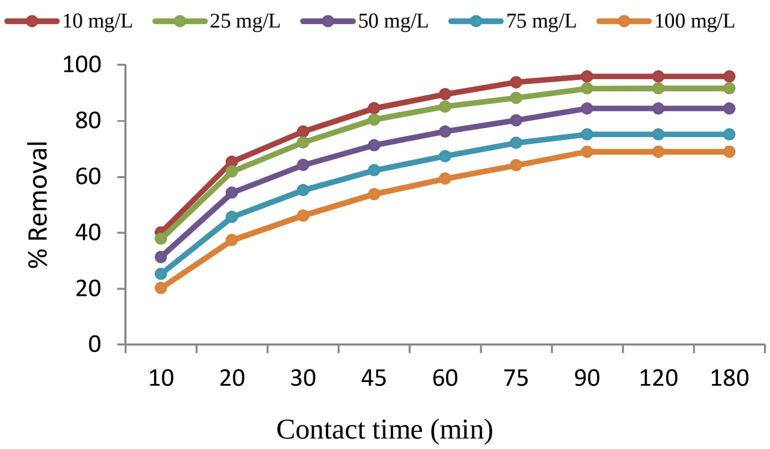

Fig 1. Effect of contact time and concentration on Cd (II) removal (pH =7, dose= 3 g/L and temp = 30± 2◦C)

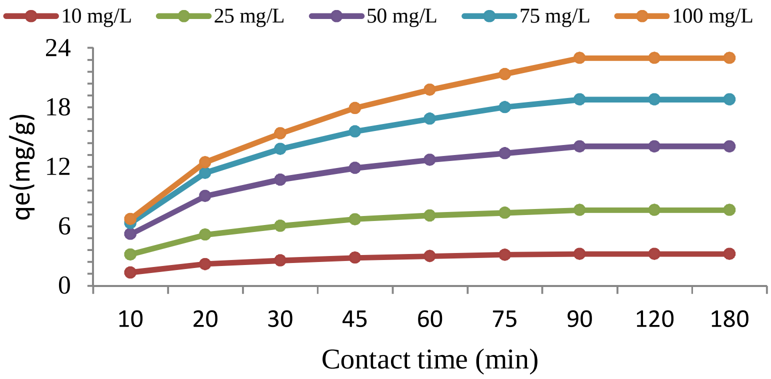

Fig 2. Effect of contact time on adsorption capacity (pH =7, dose =3 g/L and temp = 30± 2∘C)

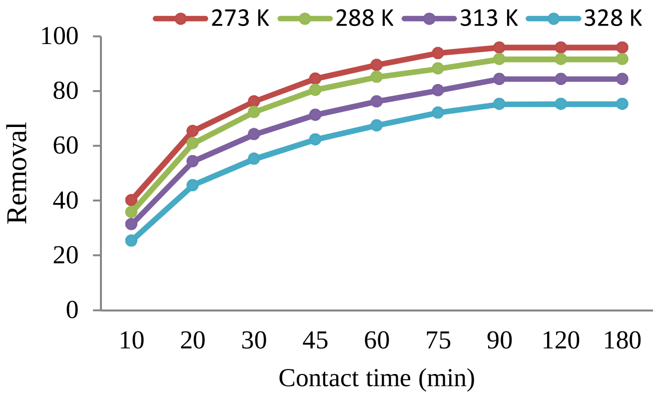

Fig 3. Effect of temperature on Cd (II) removal (pH =7, dose= 3 g/L and temp = 30± 2∘C and C_0= 10 mg/L)

CONCLUSION

Agricultural waste is an effective adsorbent for removing various heavy metal contaminants. In this study, barley husk were used to investigate the removal of Cd(II) in the concentration range of 10–100 mg/L. Increasing the temperature decreased the cadmium adsorption rate, but the maximum adsorption capacity was similar. Thermodynamic analysis showed that the adsorption process was exothermic and spontaneous in nature.

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