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Original Research Paper

Removal of Cd(II) Ions from Aqueous Solutions onto Modified Sesame Husk

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ABSTRACT

One of the important sources of environmental pollution is heavy metals of industrial wastewater which are harmful for human health and environment. Therefore, the purpose of this research was to investigate the removal of Cd from aquatic solution by tartaric acid modified sesame husk. This research was an applied and experimental type. The effects of pH, initial adsorbent concentration, initial metal ion concentration and contact time were studied in batch experiments. The result showed that the Cd removal efficiency increased by increase in adsorbent dosage, pH (up to 5) and contact time and decrease in Cd concentration. In optimum condition, modified sesame husk removed 99% of Cd from aqueous solutions. The equilibrium data were best fitted on Freundlich isotherm and the adsorption kinetic model followed a pseudo-second model. ANOVA showed that there was a significant difference between variables and Cd removal. According to the results obtained, modified sesame husk appears to be suitable, low cost and efficient adsorbent for removing Cd from aqueous solutions.

INTRODUCTION

The presence of heavy metal water has generated major concern in recent years. Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations and tanneries. Among the toxic heavy metal ions which present potential danger to human health are copper, lead, cadmium, chromium and mercury. These heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders (Bulut & Baysal 2006). Heavy metals are conventionally defined as elements with metallic properties and an atomic number >20 (Tangahu & Abdullah 2011). Cadmium is one of the heavy metals, which is highly toxic to human, plants and animals. The metal is of special concern because it is non-degradable and therefore persistent. According to WHO's recommendation Cd(II) limit in drinking water is 0.005 mg/L (Rao et al. 2010). Many methods have been developed to treat wastewater polluted by heavy metals, including chemical precipitation, ion exchange, electrolysis, coagulation and membrane separation, but these methods have disadvantages such as secondary pollution, high cost, high energy input, large quantities of chemical reagents or poor treatment efficiency at low metal concentration. A promising alternative is biosorption, since it has high efficiency and low cost, wide adaptability and selectivity in removing different kinds of heavy metals, and stable performance in purifying wastewater of low metal concentrations (1–100 mg/L) (Sud & Mahajan 2008, Wang & Chen 2009, Farooq et al. 2010). Although various types of biomass, such as fungi, bacteria, yeast and algae, have been investigated under laboratory conditions, natural agricultural by-products have the most potential as natural sorbents for heavy metal detoxification of large-scale effluent, due to their low cost, abundance, reliability and availability (Ding et al. 2012).

Agricultural materials, particularly those containing cellulose shows potential metal biosorption capacity. The basic components of the agricultural waste materials, biomass, include hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, starch containing a variety of functional groups that facilitate metal complexion which helps for the sequestering of heavy metals (Sud et al. 2008). Many low cost agricultural waste materials, such as canola, banana stem, rice husk, sawdust, maize bran, walnut shell, tree fern, wheat bran, tree leaves, cashew nut shells, nettle ash, almond husk, wheat bran and corncob tea factory waste, wheat and rice straw, have been used for the removal of heavy metals (Gao et al. 2008, Gong et al. 2008).

The aim of this work is to study Cd(II) ions adsorption from aqueous solutions onto the modified sesame husk as a cheap agricultural waste material. Different factors affecting the adsorption such as the initial solution pH, contact time, adsorbent dosage and initial metal ion concentration on the adsorption isotherm were examined to optimize the adsorption process. The biosorption equilibrium and kinetic data are fitted using different models and process parameters were evaluated.

MATERIALS AND METHODS

Preparation of adsorbent: The sesame husks used in the present investigation were procured locally from Mazandaran province in Iran. Rice hull was washed thoroughly with water to ensure the removal of dust and ash. It was then rinsed several times with distilled water and dried overnight in an oven at 50 °C. The dried sesame husk was then ground to pass through a 1 mm sieve. For modification, about 5 g ground sesame husk was mixed with 35 mL of 1.2 M tartaric acid (TA). The mixture was stirred until homogeneous and dried at 50°C overnight. The treated sesame husk was subsequently washed with distilled water until neutral and dried overnight at 50°C (Ong et al. 2010).

Batch adsorption: The adsorption experiments were carried out in a batch process. The literature review indicated that the most important effective variables on adsorption, include pH, adsorbent dose, and contact time and Cd concentrations. Therefore, the initial Cd concentration was selected (10-150 mg/L). The effect of adsorbent dosage, contact time and pH were studied in a range of (1-6 g/L), (5-180 min) and (2-7), respectively. The experiments in batch system were carried out in a 100 mL Erlenmeyer flask Meyer. In every experiment, a certain concentration of Cd and specific dose of absorbent spilled into the flask and completely mixed with shaker at 120 rpm for 180 minutes. Then the sample was filtrated and finally, the residual concentrations were measured using Atomic Absorption Spectrometer (AAS). The amount of adsorbed Cd and removal percentage (R %) of cadmium was calculated according to the following Eq. 1 and 2.

$$q_e = \frac{(C_o - C_e)v}{m} \quad ...(1)$$

$$R(\%) = \frac{C_0 - C_e}{C_o} \times 100 \quad ...(2)$$

Where, q_e is the amount of adsorbed Cd per unit mass of adsorbent (mg/g), C_0 and C_e are the initial and the equilibrium concentrations of Cd solution (mg/L), respectively. *V* is the volume of Cd (L), and *m* is the mass of the adsorbent.

Adsorption isotherms and kinetics: Experimental isotherm is useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application, for selection of the most appropriate sorbent, and for preliminary determination of sorbent dosage requirements. Moreover, the isotherm plays an important role in the predictive modelling procedures for analysis and design of sorption systems. The Langmuir model is based on the hypothesis that there is a monolayer sorption between gas-solid phases and it is applicable to short sorption of a single heavy metal. The Freundlich model is a semi-empirical equation that may be used to describe surface sorption and multi-layer sorption under various non-ideal conditions. The Temkin isotherm model assumes that the adsorption energy decreases linearly with the surface coverage due to adsorbent-adsorbate interactions. Kinetic models are used to examine the rate of the adsorption process and potential rate controlling step (Kumar & Sivanesan 2006). In the present work, the kinetic data obtained from batch studies have been analysed by using pseudo first-order, pseudo second-order, intra particle diffusion and Elovich model. The linearized form of adsorption isotherms and kinetics is given in Table 1.

Table 1: The equations of isotherms and kinetics.

Isotherms	Langmuir 1	$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{1}{q_m} C_e$
	Langmuir 2	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_L q_m} \frac{1}{C_e}$
	Langmuir 3	$q_e = q_m - (\frac{1}{k_L}) \frac{q_e}{C_e}$
	Langmuir 4	$\frac{q_e}{C_e} = k_L q_m - k_L q_e$
	Freundlich	$Log q_e = 1/n \log Ce + \log K_F$
	Tekmin	$qe = B_1 \ln (k_t) + B_1 \ln (Ce)$
kinetics	pseudo first order	$\log(q_e - q_t) = \log q_e - (\frac{k_1 t}{2.303})$
	pseudo second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$
	Intra particle diffusion	$\log q_t = \log k_i + 0.5 \log t$
	Elovich	$q_e = C + k_e \ln t$

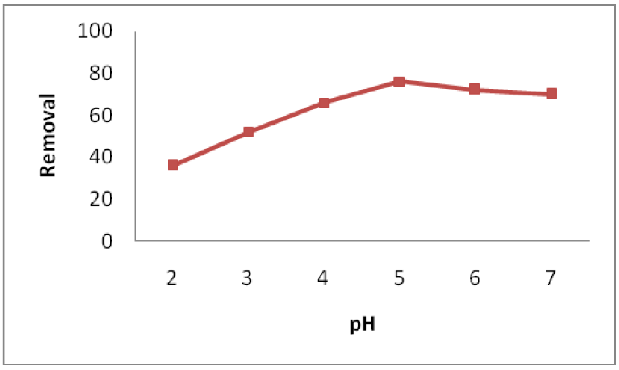

Fig. 1: The effect of pH on Cd removal efficiency (time = 120 min, Cd concentration = 50 ppm, adsorbent dosage = 0.3 g/100cc).

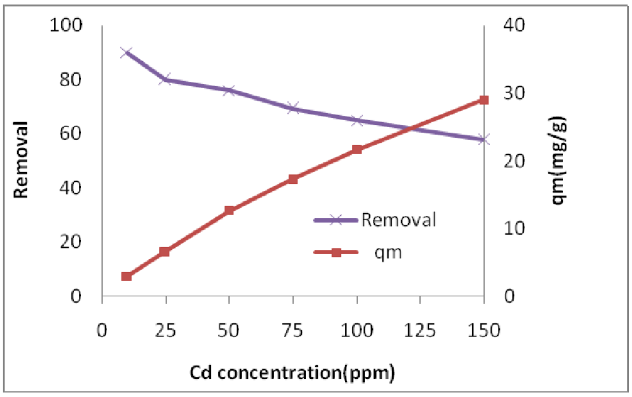

Fig. 3: The effect of Cd concentration on removal efficiency(time = 60 min, pH = 5, adsorbent dosage = 0.3 g/100cc).

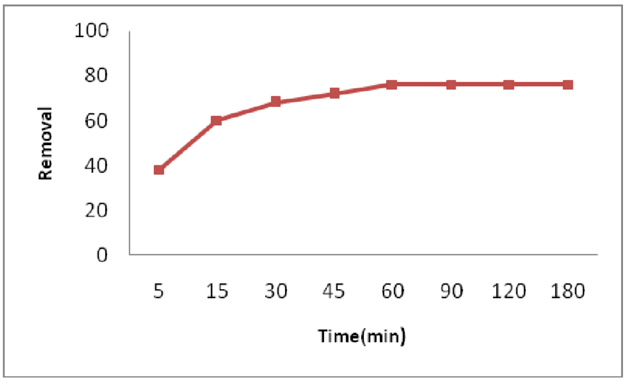

Fig. 2: The effect of time on Cd removal efficiency (pH = 5, Cd concentration = 50 ppm, adsorbent dosage = 0.3 g/100cc).

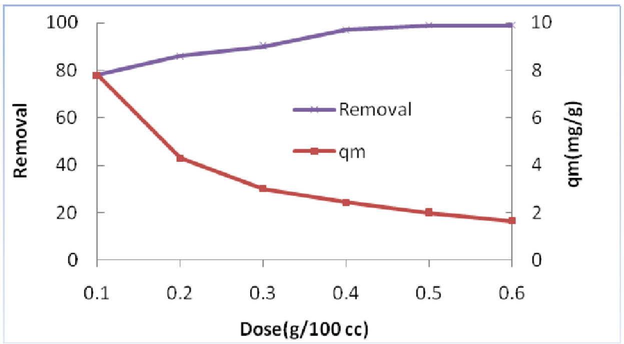

Fig. 4: The effect of adsorbent dose on removal efficiency (time = 60 min, pH = 5, Cd concentration = 10 ppm).

RESULTS

Effects of pH and contact time on the rate of adsorption of Cd by the modified sesame husk: Fig. 1 shows that the pH can influence on Cd removal percentage. The results of this experiment show that the adsorption efficiency increased by increasing of pH upto 5. However, it decreased by increasing the pH more than 5. Therefore, the optimum pH was 5. According to quadratic regression analysis it can be concluded that there was a significant difference between pH and Cd removal (Pv = 0.002).

As shown in Fig. 2, the removal of Cd increased as the contact time increased (5-60 min). After 60 min equilibration time, its rate became constant (60-180 min). Quadratic regression analysis showed that there was a significant difference between contact time and Cd removal (Pv = 0.023).

Effects of adsorbent dose and Cd concentration: Fig. 3 shows the effect of initial Cd concentration on Cd removal percentage. The results show that the Cd removal efficiency decreases by increasing Cd concentration from 10 to 150 mg/L. As shown in this figure, the Cd removal percentage is 90% for Cd concentration of 10 mg/L. It decreases to 58% for the concentration of 150 mg/L. Quadratic regression analysis showed that there was a significant difference between initial Cd concentration and the Cd removal rate (Pv = 0.003).

The effect of adsorbent dose varying from 1 to 6g/L on the percentage removal of Cd was studied and shown in Fig. 4. The adsorption efficiency increased by increasing the adsorbent dose upto 5 g/L. However, the Cd removal reaches to balance in concentrations more than 5 g/L. Although the adsorption efficiency increases with increase in adsorbent dose, however, the adsorption rate per gram of adsorbent dose (q_e) decreases. According to quadratic regression analysis, it can be concluded that there was a significant difference between adsorbent dose and Cd removal rate (Pv = 0.001).

Adsorption kinetics and isotherms: The isothermal models and adsorption kinetics are shown in Fig. 5 and Table 2.

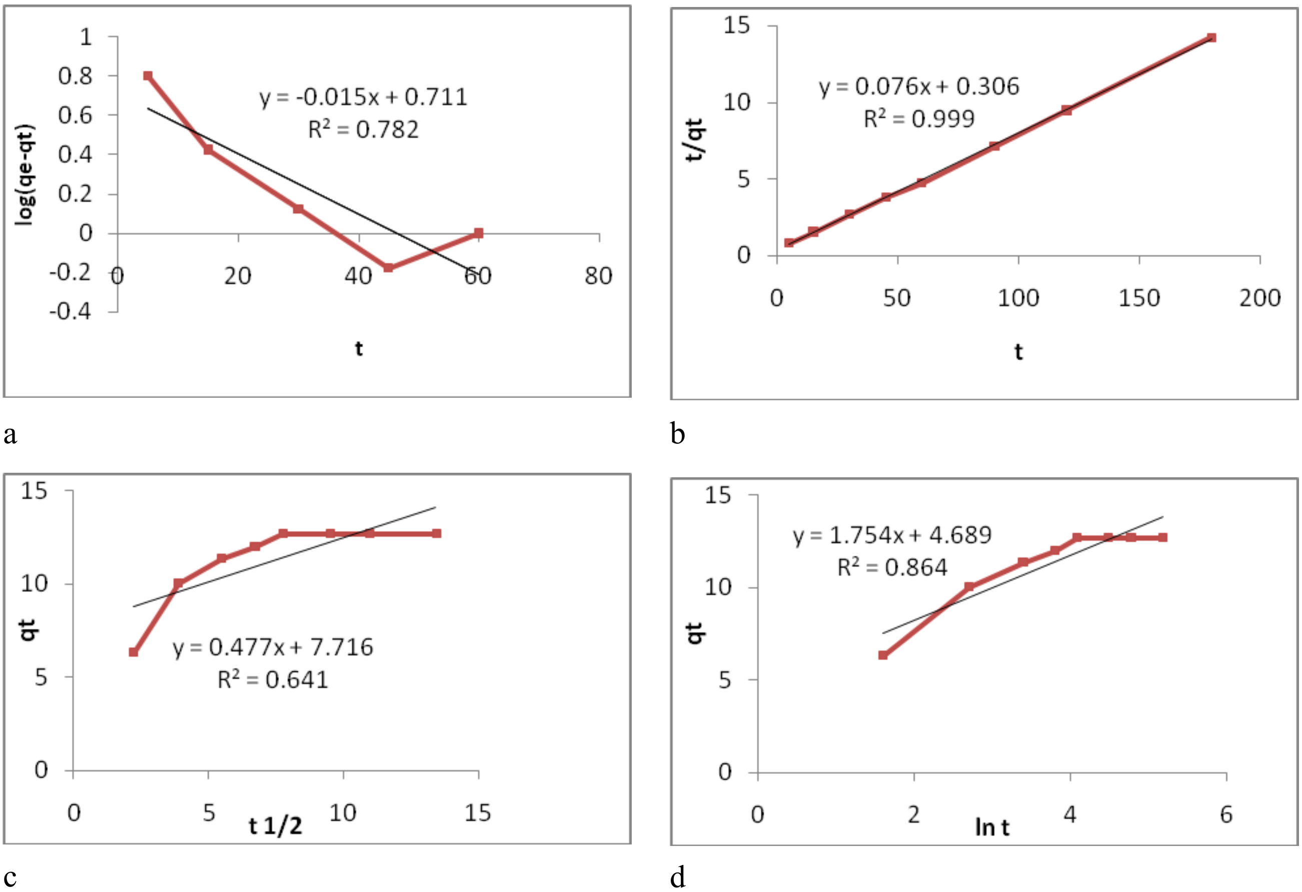

Fig. 5: The kinetics's models (a: pseudo first order b: pseudo second order c: Intra particle diffusion d: Elovich).

DISCUSSION

Pretreatment methods using different kinds of modifying agents such as base solutions (sodium hydroxide) mineral and organic acid solutions (hydrochloric acid, phosphoric acid, tartaric acid, citric acid, thioglycollic acid), organic compounds (ethylene diamine, formaldehyde), etc. (Han et al. 2010). Tarley et al. (2004) found that adsorption of Cd increased by almost double when RH was treated with NaOH. The reported adsorption capacities of Cd(II) were 7 and 4 mg/L for NaOH-treated and unmodified RH, respectively. Zhu et al. (2008) studied the soybean straw which was water or base (0.1 M NaOH) washed and CA modified to enhance its natural adsorption capacity. The amount of Cd(II) adsorbed by soybean straw increased after modification with CA, regardless of whether the samples were base washed or water washed. This was because of the increase in carboxyl groups imparted onto the straw by reaction with CA (Zhu et al. 2008). This research investigated the removal of Cd from aquatic solution by tartaric acid modified sesame husk, that showed increase in the adsorption efficiency. The introduced free carboxyl groups of TA increase the net negative charge on the sesame husk, thereby increasing its binding potential for cationic contaminants (Zhu et al. 2008). The pH solution is an important parameter for removal of pollutants from water solutions. As shown in Fig. 1, maximum adsorption of cadmium has taken place at pH 5. At low pH (< 2.0) the biosorption capacity for all metal ions is very low, because large hydrogen ions compete with metal ions at sorption sites. As the pH (from 3.0 to 5.0) increases, more negatively charged cell surface becomes available, thus facilitating greater metal uptake (Yun-guo et al. 2006). The effect of contact time on the adsorption of cadmium ions by modified sesame husk is shown in Fig. 2. It is observed that the adsorption process is rapidly increasing at the beginning. However, it decreases and reaches equilibrium after 60 min, this can be described by the presence of the most active sites on the surface area of the adsorbent and the saturation of these sites by Cd with time (Singh et al. 2005). The adsorption efficiency decreased by increase in the initial concentration of Cd, however the adsorption capacity increased. This probably occurs due to the fact that by increasing the

Table 2: The adsorption isotherms constants for Cd removal.

	R^2	q_m	k_l	k_f	k_t	n	B_l
Langmuir 1	0.948	37	0.049	-	-	-	-
Langmuir 2	0.962	20	0.172	-	-	-	-
Langmuir 3	0.891	56.23	0.015	-	-	-	-
Langmuir 4	0.891	64.84	0.013	-	-	-	-
Freundlich	0.996	-	-	2.94	-	1.78	-
Tekmin	0.909	-	-	-	1.03	-	6.12

surface charge on the adsorbent, the adsorption sites of top surfaces of adsorbent are saturated and the removal efficiency decreased (Garg et al. 2008). The adsorption rate increased with the increasing adsorbent dose which it is due to increase of the active surface of adsorbent. The results showed that although efficiency increased with increasing adsorbent dose, however, the Cd adsorbed per gram of adsorbent decreased because the active sites of adsorbent are not saturated. With the increase in adsorbent dose, the total capacity of the adsorbent surface points is not used completely and this reduces the absorption rate per unit mass of the adsorbent (Yousefi et al. 2011). Lower biosorption capacity of Cd at a higher dosage of biosorbent is probably due to the decrease of the surface area of the biosorbent by the overlapping or aggregation during the sorption (Anwar et al. 2010). The R^2 of kinetic models suggested that the pseudo second-order model mechanism is predominant. It means, the uptake process follows the pseudo-second-order expression with correlation coefficients always greater than 0.99. The correlation coefficient (R^2) for Freundlich equation always greater than 0.99, which was slightly more than the R^2 value, obtained from the others equation, indicating that the Freundlich model better fitted the equilibrium obtained in this study. From Table 2 the 'n' value of Cd(II) was observed to be more than the value of 1, thus indicating that the adsorption is favourable for the removal of Cd(II) by modified sesame husk. Therefore, the adsorption process is based on the hypothesis of multi-layer biosorption.

CONCLUSION

The present study shows that the tartaric acid modified sesame husk is an effective adsorbent for the removal of Cd from aqueous solutions. The reduction rate Cd aqueous solutions were more than 99% at optimal conditions. Adsorption equilibrium follows Freundlich isotherm. Kinetics of adsorption follows pseudo second-order model.

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