

Cadmium Removal from Aqueous Solutions Using Saxaul Tree Ash

Sanchooli Moghaddam, Marziyeh

Health Center of Zabol, Zabol University of Medical Sciences, Zabol, I.R. IRAN

Rahdar, Somayeh

Department of Environmental Helth, Zabol University of Medical Sciences, Zabol I.R. IRAN

Taghavi, Mahmoud*⁺

Department of Environmental Health Engineering, Gonabad University of Medical Sciences, Gonabad, I.R. IRAN

ABSTRACT: Cadmium can be found in wastewater in high concentrations and can cause dangerous effect on aqueous environment and human health. At present, many methods have been used to heavy metals removal. Among this clean up techniques, adsorption techniques by using low-cost adsorbent are more considerable. In this study, batch adsorption experiments were conducted for removal of cadmium ions from aqueous solutions by using saxaul tree ash as a low-cost adsorbent. The batch experiments were conducted in various conditions as follows: pH (3 to 11), adsorbent dose (0.5 to 6 g/L) g, contact time (15 to 210 min), and initial cadmium concentration (5-50 mg/L). Based on the results, pH=5 with an adsorbent dose of 4 g/L with a 75 min contact time were found to be the optimum for adsorption of cadmium on saxaul tree ash. Also, the results showed that adsorption efficiency is decreased with increase in initial concentrations of cadmium. The isotherm experiments showed that Freundlich model satisfactorily represents the proportional fitting. Therefore, base on the results of this study, saxaul tree ash can be used for efficient removal of cadmium ions from aqueous solution.

KEYWORDS: Cadmium; Adsorption; Heavy metal removal; Saxaul tree ash.

INTRODUCTION

The presence of heavy metals in aquatic environment has been of great concern, because of their toxicity for animals, plants, human, and nonbiodegradable nature [1-4]. At least, 20 metals are classified as toxic and half of these metals are emitted into the environment in quantities that pose risks to human health [5, 6]. These metals are toxic even at very little concentrations [7, 8]. Cadmium is one of the most toxic metals affecting the environment. Mining and metallurgy of cadmium,

cadmium electroplating, fossil fuels, pigments, plastic, battery, alloy manufacturing, and ceramic industries waste waters contain undesired amounts of Cd(II) ions [9, 10]. Chronic exposure to Cd(II) can affect the nervous system, liver, cardiovascular system, bones, and may lead to renal failure and death in mammals and humans [11]. It also interferes with the normal functioning of various metallo-enzymes [7, 12]. Cadmium ions can replace Zn(II) ions in some metallo-enzymes, thereby affecting

* To whom correspondence should be addressed.

+ E-mail: taghavi66@yahoo.com , taghavi66@ssu.ac.ir
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the enzyme activity[7, 13]. The adverse effects of cadmium on humans include high blood pressure, kidney damage, destruction of testicular tissues and red blood cells[7]. Cadmium has been classified as a human carcinogen and teratogen impacting lungs, kidneys, liver, and reproductive organs[14]. US Environment Protection Agency has also classified Cd(II) as group B₁ carcinogen[13]. The World Health Organization (WHO) has set a maximum guideline concentration of 0.003 mg/L for Cd(II) in drinking water[14, 15]. The permissible limit for Cd(II) in drinking water in China and guideline value recommended by World Health Organization, is 0.005 mg/L[16]. Many physicochemical methods have been proposed for the removal of cadmium from industrial effluents [6, 17]. The methods commonly used for the treatment of waste water to remove heavy metals include chemical precipitation, chemical oxidation, filtration, electrochemical treatment, lime stone precipitation, ion exchange, reverse osmosis, membrane separation, and adsorption[17-19]. Each of the methods has its own benefits and limitations[7, 19]. Among the various water-treatment techniques described, adsorption due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness is generally preferred for the removal of heavy metal ions[20]. Commercial activated carbon is a preferred adsorbent used to remove impurities from liquid solutions; however, its widespread use is restricted due to its high cost. Activated carbon is an expensive adsorbent, especially for developing countries[21]. Recently, there is growing interest in using low cost, non-conventional alternative materials which used to be considered as waste[16, 20, 22, 23]. The use of agricultural residues or industrial by-product as alternative adsorbent for activated carbon has therefore received considerable attention[21]. Many materials, such as waste red mud and fly ash, tea-industry waste, calcite and hydroxyapatite, waste materials as refuse concrete, waste paper and charcoal, and natural indigenous rocks as andesite, limestone, granite and nitrolite, olive cake, bagasse fly ash, and rice husk ash, the orange barks, the algae, plants dried and olive stone waste have been tested for Cd(II) removal from water systems by various researchers[21, 24-26]. In this work, the adsorption behavior of cadmium ion from aqueous solution using saxaul tree ash was studied via a set of experiments at various conditions, including

solution pH, agitating time, and cadmium ion concentration and two commonly used isotherm models, which are Langmuir and Freundlich, have been applied to the experimental data.

EXPERIMENTAL SECTION

Preparation of solutions

Stock solution of Cd(II) ions with a concentration of 1000 mg/L was prepared by dissolving Cd(NO₃)₂·4H₂O (analytical reagent grade) in distilled water. The desired Cd(II) concentrations were prepared from the stock solution by making fresh dilutions for each sorption experiment and the experimental solutions were obtained by diluting the stock solution to the required concentrations (5 to 50 mg/L). The solution pH (3, 5, 7, 9, and 11) was adjusted with 0.1 M HCl or 0.1 M NaOH.

Adsorbent preparation

The stems of saxaul tree were obtained from Sistan and Blochestan province, Iran. These materials were firstly washed with distilled water to remove impurity such as sand and leaves and soluble and colored components, dried at 110°C for 12 h, burned at 700°C for 2 h, crushed in a domestic grinder, and sieved to obtain a particle size in the range of 60 to 200 mesh. The powdered adsorbent was stored in an airtight container until use. No other chemical or physical treatments were used prior to adsorption experiments.

Analysis

The residual cadmium concentration in the solutions was determined by a Varian AA-7000 atomic absorption spectrometer. The pH of the solution was measured using a pH meter (E-623).

Batch adsorption experiments

All experiments were carried out in batch system. The effect of experimental parameters, such as pH, adsorbent dosage, cadmium concentration, and contact time was evaluated in room temperature (23 ± 2°C). In each test, some 100 mL conical flasks containing cadmium were used. The operational parameters were optimized in several steps and in each step, one parameter was varied while other parameter was kept constant. For example, the effect of solution pH on the adsorption capacity of saxaul tree ash was investigated using a 100 mL solution

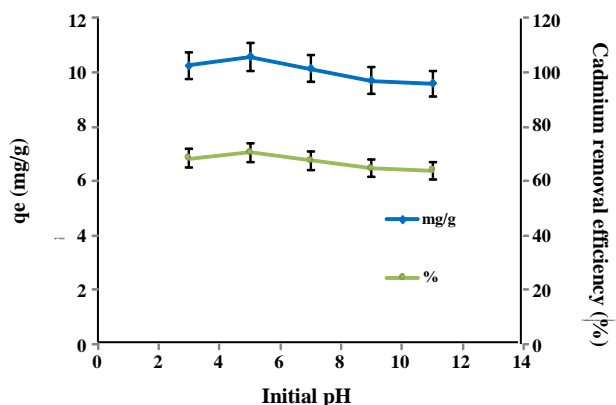


Fig. 1: Effect of pH on the adsorption of Cd(II) onto Saxaul tree ash (the initial Cd(II) concentration=30 mg/L, adsorbent dose=2 g/L, and contact time=90 min).

of 30 mg/L of Cd(II) containing 0.2 g adsorbent for a pH range of 3 to 11 in 90 min contact time. For each experiment, flasks were agitated on a rotary shaker at 225 rpm. After optimum contact time, the mixtures were filtered through Whatman 45 filter paper and the concentration of Cd(II) in the filtrates was analyzed using a 7000 atomic absorption spectrometer. The cadmium concentration determination was repeated three times and the average value was taken.

The amount of sorption, q (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of Cd(II) (mg/L), respectively, V is the volume of the solution (L), and M is the amount of adsorbent used (g/L). To express the percent of Cd(II) removal, the following equation was used:

$$\% = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

where C_0 and C represent the initial and final (after adsorption) Cd(II) concentrations, respectively (32).

RESULTS AND DISCUSSION

Effect of pH

Removal efficiency of heavy metal from aqueous solution using adsorption process strongly depends on applying the process in the optimum condition. Hence, each of the important operational parameters including pH, adsorbent dosage, contact time and cadmium concentration

were optimized in several steps. As at each step, one parameter was varied while other parameters were kept at constant value. In first step, the pH was optimized.

The removal of pollutants from aqueous environments by adsorption is greatly influenced by the pH of the solution which affects the nature of the surface charge of the adsorbent and the extent of ionization and speciation of the heavy metal species, and consequently, the rate of adsorption. On the other hand, the solution pH would affect both aqueous chemistry and surface binding-sites of the adsorbent. Therefore, the pH of the solution is one of the most critical parameters in the adsorption of pollutants from aqueous solutions. At first, increase of pH from 3 to 5 resulted in increase of cadmium adsorption from 68.3 to 70.5%. After this value, cadmium adsorption decreased with increase of the initial pH. Thus, the maximum adsorption removal of cadmium by saxaul tree ash occurred at pH 3 to 5. Nevertheless, the highest adsorption has taken place at pH 5.0 (70.49%, 10.57 mg/g) which was chosen as an optimum pH condition for further experiments.

Effect of adsorbent dose

Batch adsorption experiments were done at a different saxaul tree ash dosage ranging from 0.05 to 0.6 g in a 100 mL solution of 30 mg/L of Cd(II) at pH 5.0 for a contact time of 80 min. Effect of adsorbent dosage was shown in Fig. 2. The adsorption efficiency of Cd(II) increased very quickly with an increase in dosage of saxaul tree ash from 0.5 to 4 g/L. A very slight increase of cadmium removal was observed with further increase in the adsorbent dose. In other word, adsorption efficiency reached to equilibrium at 0.4 g/L adsorbent dosage. Contrary to adsorption efficiency, the maximum adsorption capacity was decreased from 38.92 to 7.43 mg/g by increase of adsorbent dosage from 0.5 to 4 g/L. This is expected because higher dose of adsorbent in the solution resulted in the greater availability of active sites for the ions adsorption[27].

Effect of contact time

The effect of contact time on adsorption of cadmium was studied at different contact times (15 to 210 min) for an initial concentration of 30 mg/L of Cd(II) solution containing 4 g/L at pH 5. As shown in Fig. 3, the adsorption capacity and the removal efficiency of Cd(II)

onto the saxaul tree ash rapidly increase during the first 30 min of contact time. An increase of adsorption efficiency with a gentle slope was observed with further increase in contact time. In the initial stages, the removal efficiency of the metal ion using the sorbent increased rapidly due to the abundant availability of active binding sites on the sorbent and with gradual occupancy of these sites, the sorption became less efficient in the later stages. The results showed that more than 80% of the sorption capacity of saxaul tree ash for cadmium is achievable within the first 75 min of contact time. Beyond this point, the removal further increased but with a slower rate. Thus, this time was chosen as contact time for the next experiment.

Effect of initial Cd(II) concentration

In order to survey the effect of initial cadmium concentration on adsorption efficiency, batch experiments were carried out by a series of 100 mL of cadmium solutions with different cadmium concentrations of 5, 10, 20, 30, 40 and 50 mg/L containing 0.4 g/L of adsorbent dosage at pH value of 5. As shown in Fig. 4, when the initial cadmium concentration is increased, the equilibrium concentration of cadmium is also increased. In other words, decreased adsorption efficiency is caused by increase in initial cadmium concentration. The removal efficiency was decreased from 88.01 to 74.48% with increase in initial cadmium concentration from 5 to 50 mg/L. At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of cadmium ions. Therefore, the amount of cadmium adsorbed on adsorbent increases with increase of cadmium concentration which indicate that the saturation of adsorbent has not achieved in this range of cadmium concentration [28]. However, at higher concentration, the number cadmium ions are relatively higher as compared to the available adsorption sites which resulted in decrease in the removal efficiency and consequently increase in equilibrium cadmium concentration in the solution.

Isotherms study can describe how an adsorbate interacts with adsorbent. The isotherm provides a relationship between the concentration of Cd(II) in solution and the amount of Cd(II) adsorbed on the solid phase when both phases are in equilibrium. The equilibrium adsorption data were analyzed by using the Langmuir and Freundlich isotherm models [8, 29, 30].

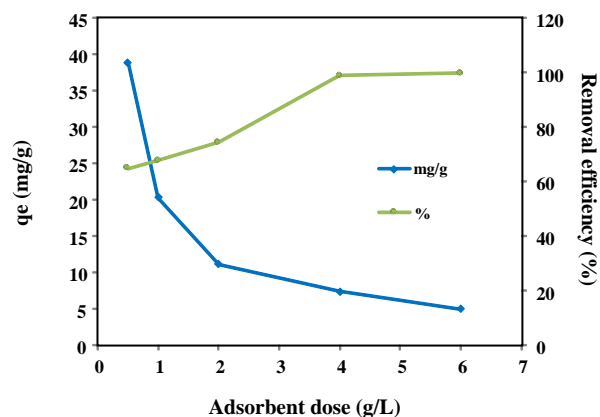


Fig. 2: Effect of adsorbent dose on the adsorption of Cd(II) onto Saxaul tree ash (the initial Cd(II) concentration = 30 mg/L, pH=5, and contact time=90 min).

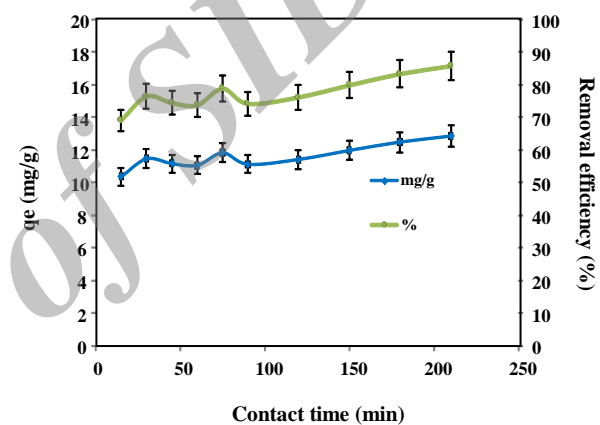


Fig. 3: Effect of contact time on the adsorption of Cd(II) onto Saxaul tree ash (the initial Cd(II) concentration = 30 mg/L, pH = 5, and adsorbent dose = 4 g/L).

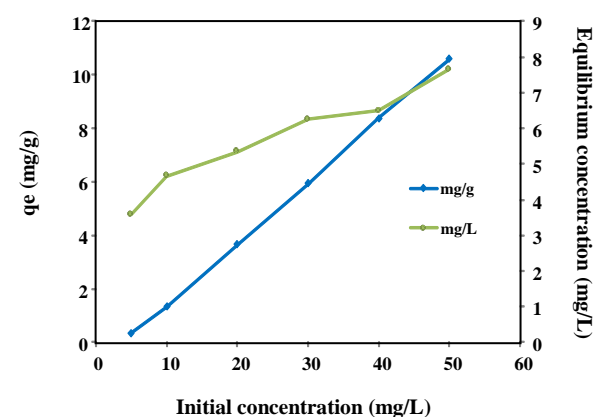


Fig. 4: Effect of initial Cd(II) concentration on the adsorption of Cd(II) onto Saxaul tree ash (adsorbent dose = 4 g/L, pH = 5, and contact = 75 min).

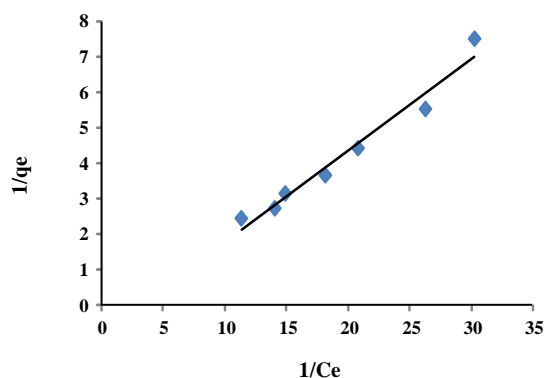


Fig. 5: The Langmuir isotherm for adsorption of Cd(II) onto saxaul tree ash.

The Langmuir isotherm model is valid for monolayer adsorption onto surface containing a finite number of identical sorption sites which is presented by the following equation:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

where q_e is the amount of metal adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration of the solution (mg/L), and q_m is the maximum amount of Cd(II) required to form a monolayer (mg/g). Langmuir equation can be rearranged to a linear form for the convenience of plotting and determining the Langmuir constants (b) and the maximum monolayer adsorption capacity of saxaul tree ash (q_m). The values of q_m and b can be determined from the linear plot of $1/q_e$ versus $1/C_e$:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b} \frac{1}{C_e} \quad (4)$$

where q_e is the sorption capacity of adsorbent at equilibrium (mg/g), q_m and b are the maximum cadmium ions adsorbed per unit mass of the adsorbent (mg/g) and Langmuir constant, in relation to energy of sorption which quantitatively indicates the affinity between the adsorbent and cadmium ions (L/mg), respectively [31].

The favorable or unfavorable of the adsorption system can be determined based on the essential characteristic of the Langmuir model which can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is defined as follows:

$$R_L = \frac{1}{1 + b C_e} \quad (5)$$

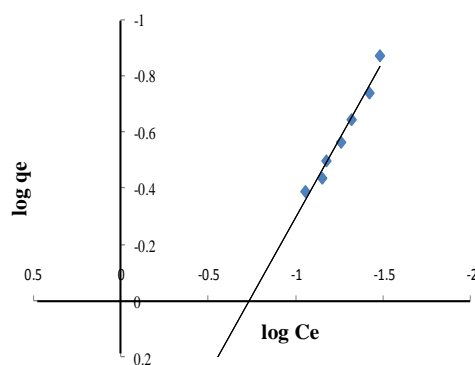


Fig. 6: The Freundlich isotherm for adsorption of Cd(II) onto Saxaul tree ash.

where b and C_0 show the Langmuir constant and the initial concentration of cadmium. According to the values of R_L , the shape of the isotherm can be shown to be irreversible ($R_L=0$), favorable ($0 < R_L < 1$), linear ($R_L=1$) and unfavorable ($R_L > 1$) [32].

The adsorption intensity of the cadmium ions towards the adsorbent can be determined using the Freundlich model [33]. The Freundlich equation is purely empirical based on sorption on heterogeneous surface, which is commonly described by the following equation:

$$q_e = K_f C_e^{1/n} \quad (6)$$

Where q_e is the sorption capacity of adsorbent at equilibrium (mg/g), K_f and $1/n$ are the Freundlich constants in relation to adsorption capacity and adsorption intensity, respectively. The Freundlich equilibrium constants were evaluated from the intercept and the slope, respectively, of the linear plot of $\log q_e$ versus $\log C_e$ based on experimental data. The Freundlich equation can be linearized in a logarithmic form for the determination of the Freundlich constants as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

Where the constant K_f shows the adsorption capacity and the constant n indicates the adsorption intensity. They can be determined from the plot of $\ln q_e$ versus $\ln C_e$ [27, 34, 35].

Isotherms based on the experimental data are shown in Figures 5 and 6. In addition, the calculated parameters of the Langmuir and Freundlich isotherm models for saxaul tree ash, as well as the correlation coefficients (R^2),

Table 1: Parameters for Langmuir and Freundlich isotherm models of Cd(II) adsorption on saxaul tree ash.

Isotherm model	Parameter	Saxaul tree ash
	$q_m(\text{mg/g})$	2.65
	$b (\text{L/mol})$	2.96
Langmuir	R^2	0.966
	MPSD	8.862
	HYBRID	0.251
	R_L	0.0325
	$K_f (\text{mg/g} (\text{L/mg})^{1/n})$	8.19
Freundlich	n	0.896
	R^2	0.975
	MPSD	6.986
	HYBRID	0.123

are listed in Table 1. The Freundlich models showed higher correlations than the Langmuir models. Therefore, the Freundlich adsorption isotherm is suitable for describing the adsorption equilibrium of Cd(II) onto saxaul tree ash. As mentioned earlier, k_f is the equilibrium constant indicative of adsorption capacity and higher k_f means that the adsorption capacity is higher.

In order to measure the goodness-of-fit for two isotherm models, the hybrid error function (HYBRID) and the Marquardt's percent standard deviation (MPSD) were determined by the following equations:

$$\text{HYBRID} = \frac{100}{N-p} \sum_{i=1}^N \left[\frac{(q_{e_i}^{\text{exp}} - q_{e_i}^{\text{cal}})^2}{q_{e_i}^{\text{exp}}} \right] \quad (8)$$

$$\text{HYBRID} = 100 \sqrt{\frac{1}{N-p} \sum_{i=1}^N \frac{(q_{e_i}^{\text{exp}} - q_{e_i}^{\text{cal}})^2}{q_{e_i}^{\text{exp}}}} \quad (9)$$

Where $q_{e_i}^{\text{exp}}$ and $q_{e_i}^{\text{cal}}$ are the observation from the experiment and the estimate from the isotherm for corresponding $q_{e_i}^{\text{exp}}$, respectively. N and p are the number of observations in the experimental isotherm and the number of parameters in the regression model. The smaller HYBRID and MPSD values indicate more accurate estimation of q_e value. The HYBRID and MPSD

parameters which are listed in Table 1 suggesting that Freundlich isotherm provides a better model of the sorption system [36].

CONCLUSIONS

Cadmium in water is acutely toxic and can lead to a number of health problems. In the present study, the adsorption ability of the saxaul tree ash was evaluated for Cd(II) adsorption. Batch adsorption tests demonstrate that the adsorption is affected by various conditions, such as initial pH, adsorbent dosage, contact time, and initial Cd(II) concentration. From the present study, it can be seen that saxaul tree ash can be used effectively to remove Cd(II) from aqueous solutions. This adsorbent was able to remove up to 84.7% of Cd(II) from solutions at optimum condition and 50 mg/L Cd(II) concentration. The removal of Cd(II) from aqueous solutions follows from Freundlich isotherm model. Based on the results of this study, adsorption of Cd(II) using saxaul tree ash can be a hopeful process, but more studies are needed. Therefore, it is suggested that more investigations be done on effect of interferences on adsorption of cadmium onto Saxaul tree ash as well as thermodynamic studies, effect of ionic strength and competitive effect of other heavy metal ions.

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