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Research Article

ISOTHERMS AND THERMODYNAMICS OF CD (II) ION REMOVAL BY ADSORPTION ONTO AZOLLA FILICULOIDES

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Abstract:

The sorption of Cd(II) from aqueous solutions by Azolla Filiculoides (AF) was investigated. The effects of the contact time, particle size, temperature, pH, were studied in batch experiments. The kinetics of cadmium(II) adsorption were fast with 94% of adsorption taking place within 90 min. This study demonstrated that the AF biomass could be used as an effcient biosorbent for the treatment of Cd(II) bearing wastewater streams. Maximum Cd(II) removal was observed at pH 7.0. The adsorption isotherms were described by Langmuir and Freundlich isotherm models, and isotherms studies indicated that the adsorption process was best described by the Langmuir kinetics (R^2>0.995). The monolayer adsorption capacity of AF biomass was found to be 52.44 mg/g at room temperature (25°C). These results suggest that AF biomass could be employed as an efficient adsorbent for the removal of Cd(II) from contaminated water sources.

Keywords: Cd(II) , Azolla Filiculoides, Adsorption, Isotherms.

Introduction: Rapid industrialization has led to increased disposal of heavy metals into the environment(1,2). Heavy metals are defined as those metals and metalloids generally considered to be of sufficient distribution and abundance as to be in some way environmentally or biologically significant as a toxic substance(3,4). These include metals such as lead (Pb), chromium (Cr), copper (Cu), cadmium (Cd), nickel (Ni), and zinc (Zn). Cadmium, like other heavy metals, is released into natural waters by industrial and domestic wastewater discharges(5).

Cadmium is attracting wide attention of environmentalists as one of the most toxic heavy metals(6). The major sources of cadmium release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes(7). Cd(II) has been recognized for its negative effects on the environment where it readily accumulates in living systems(4). Adverse health effects due to cadmium are well documented and it has been reported to cause renal disturbances, lung insufficiency, bone lesions, cancer and hypertension in humans.

Hence, it is essential to remove Cd(II) from water and wastewater before its transport and cycling into the natural environment(8). With better awareness of the problems associated with cadmium came an increase in research studies related to methods of removing Cd(II) from wastewater, for which a number of technologies have been developed over the years(9,10).

Many physicochemical methods have been developed for heavy metal removal from aqueous solution, including chemical coagulation, adsorption, extraction, ion-exchange and membrane separation process(11). Most of these methods have been used in industrial wastewater treatment process. But these techniques have significant disadvantages including incomplete metal removal, requirements for expensive equipment and monitoring systems, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal(12,13).

Adsorption is an alternative technique for heavy metal removal. Activated carbon is a commonly used adsorbent for the removal of pollutants present in water and wastewaters. Studies have shown that the removal of various heavy metal ions from aqueous solutions can be achieved using activated carbon. In spite of its effectiveness in the removal of heavy metals from wastewaters, the high cost of activated carbon has restricted its more widespread use. Hence, an economical and easily available adsorbent would certainly make an adsorption-based process a viable alternative for the treatment of wastewater containing heavy metals(14-17).

Azolla Filiculoides (AF) is a floating water fern which it can grows rapidly on the water surface and can form a dense mat, therefore it can lead to many negative effects to aquatic life (18,19). Therefore, use of AF as a biosorbent to remove dye from the industrial effluent can help to solve both problems including dye removal as well as weeds problem (20,21).

Recently, dried and modified AF has been used as a proper biosorbent for the removing of heavy metal(22,23), phenol compounds (24-25) and antibiotics(26) and dyes effluent (27-29).

The present work investigates the potential use of AF biomass as adsorbent for the biosorption of Cd(II) from aqueous solutions. The effects of particle size, contact time and initial Cd(II) concentration and pH on the biosorption of Cd(II) onto AF were investigated.

Materials and Methods:

Preparation of biomass

Azolla Filiculoides samples were supplied from Anzali wetland, Iran. The biomass was washed with distilled water and then dried at 60 ◦C until constant weight and stored at room temperature.

Acid pretreatment was carried out as follows: a weighed amount of dried biomass samples was treated with 0.5 M H_2SO_4 solution (200 ml) for 120 min under slow stirring. The samples were washed with distilled water until removing excess H^+ ions. The biomass was dried at 103 ◦C until constant weight. Dried biomass was broken into pieces and was separated into certain particle sizes (10 to 50 mesh) by sieve and it was used for adsorption experiments.

Biosorption experiments

Batch experiments of biosorption were performed at constant temperature (30 °C) in Erlenmeyer flasks, stirred in a reciprocal shaker (200 rpm) for 2 h. In all sets of experiments 3 g of biomass of coconut shells was thoroughly mixed into 100 ml solution of Cd(II).

After shaking the flasks, the reaction mixtures were filtered to remove particulates and the filtrates were analyzed by atomic absorption spectrophotometer for the concentration of Cd(II). The stock solution of metal was prepared in deionized water using $CdSO_4$ 8/3 H_2O.

The reagent used was analytical grade supplied by Merck. A first series of biosorption experiments were carried out with Cd(II) with an initial concentration of 50 mg/L. In these tests the optimal pH value of biosorption was determined. After this, the influence of contact time was evaluated.

The percentage removal of Cd(II) were calculated using the following relationship(30, 31):

$$R = \frac{(Co - Ce)}{C_0} \times 100$$

Where C_0 and C_e are the initial and final (equilibrium) concentrations of the synthetic solution of solution (mg/L), respectively. The amount of the synthetic solution of adsorption per unit mass of Azolla Filiculoides at equilibrium, q_e (mg/g) was calculated by the following equation(32, 33):

$$q_e = \frac{(Co - Ce) \times V}{M}$$

Where V is the volume of the synthetic solution of solution (L) and W is the weight of Azolla Filiculoides (g) added to volume V.

Results and Discussion:

Effect of pH

There is general consensus that pH is a key parameter, along with metal concentration and solution composition, in determining biosorption levels. Accordingly the objectives of this work was evaluate the biosorption of Cd(II) by AF biomass from aqueous solution and to determine the effects of pH (in the range 4–9) on uptake levels. The effect of initial pH on biosorption of Cd(II) is presented in Fig. 1. The results presented show excellent removal capacities for Cd(II)

By using AF biomass. The Cd(II) removal increased from 73.2%, at pH 4, to 94.1%, at pH 7. Above pH value of 7 the removal comes constant until pH 9; at higher values of pH cadmium ions precipitate as $Cd(OH)_2$. The dependence of metal uptake on pH is related to both the surface functional groups present on the biomass and the metal chemistry in solution(17). At low pH, the surface ligants are closely associated with the hydronium ions (H_3O^+) and restricted the approach of metal cations as a result of the repulsive force(2). Furthermore, the pH dependency on the metal ions uptake by biomasses can also be justified by the association–dissociation of certain functional groups, such as thecarboxyl and hydroxyl groups present on the biomass(15). In fact, it is known that a low pH, most of the carboxylic groups are not dissociated and cannot bind the metal ions in solution, although they take part in complexation reactions(17). Based on these results, the following experiments were performed at pH 7.

Effect of particle size

Another important parameter studied was the influence of the particle size of AF biomass used for uptake of Cd(II). This parameter presents an important influence in the process cost. The results presented in Fig. 2 show a reduction in the removal of Cd(II) with the decrease of particle size of the biomass. It is important to stress that larger particles with spherical shapes, in general, present higher external mass transfer than smaller particles(34-36). In this case, higher metal adsorption from these particles is attributed to mass transport inside the sorbent particles.

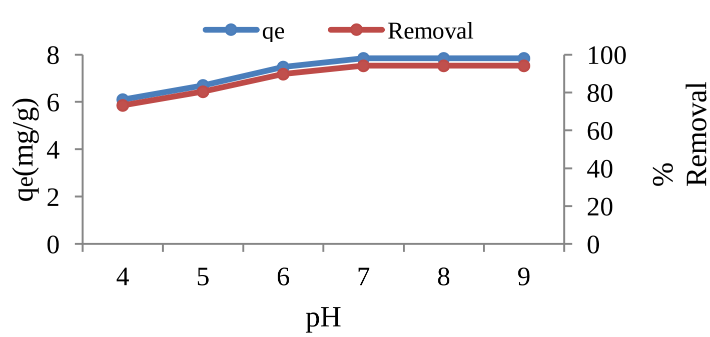


Fig 1: Effect of pH on Cd(II) adsorption. (C 0 = 25 mg/L, time = 90 min, temp= 25 ± 2∘ C and dose=3 g/L).

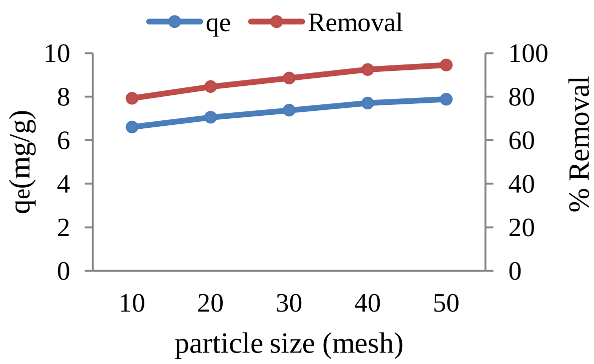


Fig 2: Effect of particle size on Cd(II) adsorption. (C 0 = 25 mg/L, time = 90 min, temp= 25 ± 2∘ C and pH=7).

Sorption isotherms

Adsorption isotherms are an important means of understanding the mechanism of an adsorption system. Hence, the biosorption of Cd(II) onto AF biomass at different temperatures of 283, 298, 313 and 328 K was determined as a function of residual (equilibrium) Cd(II) concentration (Ce).

Generally, there are two mathematical expressions commonly used to describe the isotherm of the adsorption, Langmuir and Fruendlich equations which are shown in following equations respectively(37-39):

$$\frac{Ce}{qe} = \frac{1}{q_m K_L} + \frac{Ce}{q_m}$$

$$\text{Ln } q_e = \frac{1}{n} \ln Ce + \log K_F$$

Where q_m (mg/g) is the theoretical monolayer saturation capacityor maximum adsorption and K_L is Langmuir constant related to the energy of sorption (L/g). K_F (L/mg) and 1/n are the Freundlich constants related to sorption capacity and sorption intensity respectively.

The essential quality of the Langmuir isotherm can be measured by calculating R_L a dimensionless constant referred to as the separation factor, or equilibrium parameter(40,41):

$$R_L = \frac{1}{1 + K_L C_O}$$

Where C_0 (mg/L) is the initial concentration of sorbate and K_L(L/mg) is the Langmuir constant described above. There are four possibilities for the value of R_L: for favorable sorption $0<R_L<1$, for unfavorable sorption $R_L>1$, for linear sorption $R_L=1$, for irreversible sorption $R_L=0$.

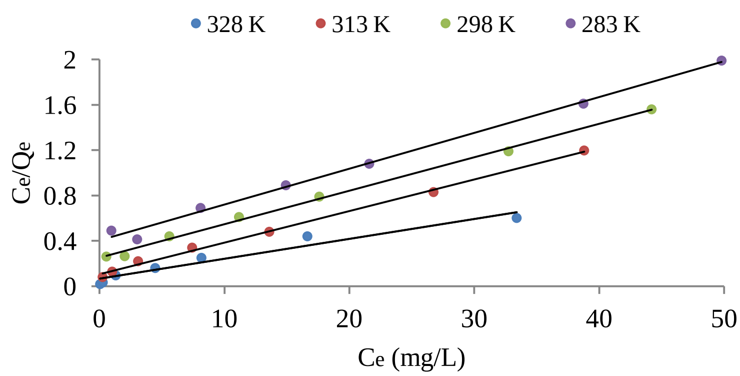
Adsorption equation parameters were obtained from experimental data by using Langmuir and Freundlich equation. The results and correlation coefficients are presented in Table 1, Fig. 3a, and Fig. 3b. By comparing the correlation coefficients R^2, it can be seen that the experimental equilibrium sorption data are better described by the Langmuir model than by the Freundlich model, with a value of R_L, lying between 0 and 1. This result suggests a monolayer coverage of the surface of AF biomass by Cd(II) ions since the Langmuir equation assumes that the surface is

Homogenous(42,43).

Other studies have also shown that the Cd(II) adsorption fits a Langmuir model(2). Moreover, the q_{max} and the K_F increase with an increase in temperature, as would be expected for sorption that is endothermic in nature.

Table 1: Isotherms constants for the removal Cd(II) onto AF biomass.

T (K)	Langmuir model				Freundlich model		
	q_m	R_L	K_L	R^2	n	K_F	R^2
283	54.28	0.282	0.049	0.998	1.325	0.419	0.942
298	52.44	0.395	0.038	0.999	1.412	0.484	0.928
313	50.89	0.446	0.026	0.997	1.879	0.567	0.937
328	48.17	0.522	0.014	0.998	2.184	0.641	0.921



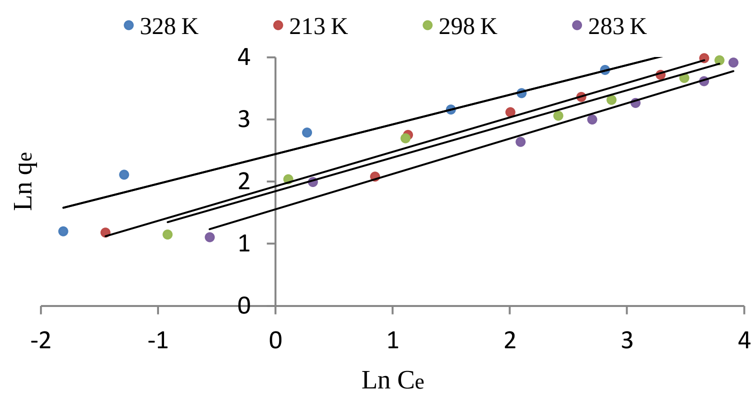


Fig. 3. (a) Langmuir isotherm model and (b) Freundlich isotherm model.

Conclusion: Azolla Filiculoides is an effective adsorbent for removing various organic and inorganic con- taminants. In this study, Azolla Filiculoides were used to investigate the removal of Cd(II) in the pH range of 4-9. The effect of temperature and equilibrium of cadmium sorption on AF biomass was thoroughly examined. Consistent with an endothermic reaction, an increase in the temperature resulted in increasing cadmium adsorption rate. The adsorption isotherm data could be well described by the Langmuir compared with Freundlich isotherm. The maximum adsorption capacity of AF biomass for Cd(II) was found to be 54.28 mg g^{-1} at 328 K.

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