Removal of Cadmium Ions from Simulated Wastewater Using Rice Husk Biosorbent

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Abstract

Biosorption of cadmium ions from simulated wastewater using rice husk was studied with initial concentration of 25 mg/l. Equilibrium isotherm was studied using Langmuir, Freundlich, BET and Timken models. The results show that the Freundlich isotherm is the best fit model to describe this process with high determination coefficient equals to 0.983. There was a good compliance between the experimental and theoretical results. Highest removal efficiency 97% was obtained at 2.5g of adsorbent, pH 6 and contact time 100 min.

Keywords: **Cadmium, Biosorption, Rice Husk, Natural Adsorbents, Isotherm Model**

ازالة ايونات الكادميوم من المياه المحضرة مختبرياً باستخدام قشور الرز كمادة مازة طبيعية

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الخلاصة:

تم دراسة عملية امتزاز ايونات الكادميوم (بتركيز 25 ملغرام \ لتر) من المزيج المحضر مختبريا باستخدام مادة طبيعية هي قشور الرز كمادة مازة. وقد استخدمت عدة موديلات لتمثيل عملية الامتزاز ووجد ان Freundlich model هو الموديل الافضل. وان كفاءة عملية الامتزاز تتأثر بشكل واضح بكمية المادة المازة و قيمة ال pH حيث وجد ان اعلى كفاءة (97 %) تم الحصول عليها عند استخدام 2.5 غرام من المادة عند 6pH وبزمن 100 دقيقة .

الكلمات الرئيسية: الكادميوم ، الامتزاز الحيوي، قشور الرز، المواد المازة الطبيعية ، التمثيل الرياضي.

1. Introduction

Among the various known forms of pollution, water pollution is of great concern, years of increased industrial, agricaltural and domestic activities have resulted in the generation of large amount of wastewater containing a number of toxic pollutants.

The presence of heavy metals in the environment is a major concern because heavy metals will not degrade into harmless end products and it is toxicity for many life forms; it is accumulate in living organisms, causing various diseases and disorders. Therefore, the elimination of heavy metals from water and wastewater is important to protect public health and ecosystem (Cheung *et al*., 2001).Cadmium is one of the principal heavy metals responsible for causing kidney damage, renal disorder, high blood pressure, bone fracture and destruction of red blood Cells

It is discharged in the effluents of many industries such as electroplating, paint pigments, plastics manufacturing, mining and metallurgical processes (Drush, 1993).

Cadmium is widely used and extremely toxic in relatively low dosages, human beings have reported nausea and vomiting at a level of 15 mg/l of cadmium, with no adverse effects at 0.05 mg/l (Kumar *et al*., 2010). The drinking water guideline value recommended by World Health Organization (WHO) is 0.005 mg Cd/l. As a resulte of the serious efforts of researchers all over the world in the field of pollution control and management a number of methodologies with varying degrees of success have been developed. 'Adsorption' is process which considered the better as compared to other methods because of convenience, easy operation, simplicity of design, and it has been shown to be an economically feasible alternative method for removing trace metals from wastewater and water supplies. Further this process can remove/minimize different types of pollutants, while activated carbon has been the most used adsorbent; nevertheless, it is relatively expensive. Cost is an important parameter for choosing the adsorbent materials

In general, adsorbent can be assumed to be low cost if it requires little processing, abundant in nature or a byproduct or waste material from another industry (Bailey *et al*., 1999).

Many materials which they are cheap and readily available sources such as coal, coke, peat, wood, or rice husk may be successfully employed for the removal of cadmium and other toxic heavy metals from aqueous solutions (Ajmal*et al*., 2003).

The utilization of agricultural waste materials is increasingly becoming important concern because these wastes represent unused resources and, in many cases, present serious disposal problems (Sun and Shi, 1998).

2 Materialand Methods

2.1 Materials (Stock Solutions)

A stock solution of cadmium ions with desired concentration was prepared by using $Cd(NO_3)_2$. Cadmium nitrate was dissolved in distilled water and analysis by atomic absorption spectrophotometer (Buck, USA).

2.2 Preparation of Biosorbent

The rice husk used was obtained from local Iraqi mill. The rice husk was crushed, sieved to 0.775 mm in diameter; and washed with distilled water to remove impurities; then dried by exposure to the sun light for 12 hr. The dried husk was stored in desiccators until used.

Table 1 Listed the physical & chemical property.

2.3 Experimental System

The different weight of adsorbent (0.1, 0.2, 0.5, 1, 2 and 2.5)g were usedto study the adsorption isotherm. The adsorbents were put in 250 ml volumetric flask with 100 ml of cadmium solution (conc. =25 mg/l). The pH of the solutions was adjusted to the pH 6 using 0.1M NaOH or 0.1M HNO_3. Thenthe flasks placed on a shaker (SM-25, Edmund bühler, Germany)and agitated continuously for 3hr at 150 rpm. The samples were filtered by filter paper (Whatman 42). The adsorbed amount was calculated by the following equation (Sulaymon*et al*., 2010):

$$q_e = \frac{V_L(C_o - C)}{W} \qquad (1)$$

Where C_o and C are the initial and equilibrium concentrations (mg/l) of cadmium solution, respectively; V_L is the volume of solution (l), and W is the mass (g) of the adsorbent

The biosorption isotherms were obtained by plotting the mass of solute adsorbed per unit mass of adsorbent (q_e) against the equilibrium concentration of the solute in the solution (C).

2.4Fourier-Transform Infrared Analysis (FT-IR)

In order to determine which functional groups were responsible for metal uptake, an FT-IR analysis in solid phase was performed on the biomass prepared in a KBr disk. FT-IR spectra were obtained for adsorbent solid samples before and after the biosorption process. Dry biomass samples were examined with the FT-IR spectrophotometer (Shimadzu FTIR 8000).

A 2.5 g of dry biomass was placed in 100 ml of Cd(II) solutions of 25 mg/l concentration. The contents of volumetric flask were adjusted to pH value of 6. The samples were shacked for 100 min at agitation speed of 150 rpm, the supernatant was discarded and the biomass was left to dry. Dried samples were collected and analysis.

2.5 Biosorption Isotherms Model

The analysis of the isotherm data by fitting them to different isotherm models is an important step to finding a suitable model that can be used for design purpose. The biosorption capacity of this system was investigated with the Langmuir, Freundlich, BET and Temkinbiosorption isotherms models.

3.1 Results And Discussion

Mass of adsorbent is one of the important parameters in biosorption processes because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. Under a given set of operating conditions this effect is explain in **Fig.1** and **2**. These figures show that the adsorption of Cd(II) increases rapidly with increasing the mass of adsorbent from 0.1 to 2.5 g with removal efficiency from 20 to 97 % .

The increase in the removal efficiency may be attributed to the fact that, with an increase in the mass of adsorbent, more adsorbent surface is available for the solute to be adsorbed. While a significant decrease in uptake was observed when the mass was increased and the maximum up take was obtained is 9 mg of Cd(II)/g of rice husk.

Also, the percentage removal of metal ion was decreased with the decrease in pH, because the competition between protons and metal ions for sorption sites on the adsorbent surface. This is due to the fact that hydrogen ions themselves are a strong competing sorbate in one hand and the contaminant decreases the negative charge of the same surface in another hand. **Fig.3** show that the percentage removal of Cd(II) was increased as the pH of the solution increased.

Although a maximum uptake was noted at a pH of 8.As the pH of the solution increased to more than 7, Cd(II) started to precipitate out from the solution (Hengpeng*et al.*, 2010). Therefore, the increased capacity of biosorption at pH more than 7 may be a combination of both biosorption and precipitation on the surface of the adsorbents. This condition is often not desirable, as the metal precipitation could lead to incorrect values of the adsorption capacity. In practice, metal precipitation generally does not produce a stabilized form of heavy metal. The precipitation can sometimes be very small in size and, upon the neutralization of the effluent from the wastewater treatment plant, the solubility of the metals increases, resulting in a re-contamination of the waste outlet stream. It is considered that adsorbents had a maximum biosorption capacity at a pH 6, if the precipitated amount is not considered in the calculation. Therefore, it will take 6 as the optimum pH for the biosorption of Cd(II) onto rice husk for the later experiment. Tangjuank*et al.* (2009) found that the optimum pH was 6 when using cashew nut shells to removal Cd(II) from water

The effect of shaking time on biosorption of Cd(II) is illustrated in **Fig. 4**. This figure indicates that the metal concentration in aqueous solution decreases rapidly at the beginning and remains nearly constant after 90 min; this is probably due to a larger surface area of the rice husk being available at the beginning.

As the surface biosorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. The increasing contact time increased the Cd(II) adsorption and it remained constant after reach equilibrium. The maximum percentage of Cd(II) removal was attained after about 100 min of shaking time. Therefore, 100 min is selected as optimum shaking times.

El-sayed, *et al.* (2010) find that at 90 min the biosorption of Cd(II) by rice straw reach equilibrium.

3.2 FT-IR Analysis of Adsorbents

The FT-IR spectra of rice husk before and after biosorption of Cd(II) was plotted to determine the vibration frequency changes in the functional groups of the adsorbent as in **Fig. 5**and**6.**

These figures show the results obtained in this study. The spectra was measured within the range of 400–4000cm^{-1}. As shown in the Figures, the spectra display a number of adsorption peaks, indicating the complex nature of the material examined. The broad, intense absorption peaks around 3760-3340 cm^{-1} are indicative of the existence of bounded hydroxyl groups (-OH). The peaks observed at 2924 cm^{-1} can be assigned to the C–H group. The peaks around 1650 cm^{-1} are due to the carbonyl C=O stretching vibration of the carboxyl groups, while the intense band at 1380 cm^{-1} are initiated by carboxylate group (-COO) stretching. The peaks ranging from 1300-1000 cm-1 are described generally to the C–O stretching vibration in carboxylic acids and alcohols. The additional peaks at 609.8–832.6 cm^{-1} can be assigned to bending modes of aromatic compounds. All these peaks in the sample after adsorption show an absorbance substantially lower than those in the raw sample and small differences in the frequency bands

The results show that Cd(II) may be adsorbed or complexed by hydroxyl, carboxylic acids and alcohol, carboxylate and carbonyl.Results show that the bands of hydroxyl groups shifted to lower frequency. The total displacements of these functional groups were, 81 for hydroxyl group, 3.85 for carbonyl group, 3.86 for carboxylate group, 11.57 for carboxylic acids and alcohols groups, and 23.14 for aromatic compound due to the biosorption of Cd(II) onto surface of biomass. The bands of functional groups shifted to lower frequency with total amount of 123.42.

Table 2 shows the main function groups before and after biomass loaded with Cd(II) ions.

These results are similar to that obtained in previous studies by Hengpeng (2010), Srivastava*et al.* (2009) and Garg*et al.* (2008).

Fig. 7 shows that the equilibrium isotherm is of a favorable type and by apply the fourth isotherm model its fined in **Fig. 8** that Freundlich model is the best fit model to describe the biosorption of Cd(II) by rice husk and the parameters and correlation coefficient of these models are show in **Table 3.**

These results were analogues to that found from Kumar *et al.*, (2010) and El-sayed*et al.* (2010) when used rice husk ash and rice straw respectively as adsorbent and Cd(II) as adsorbat.

4. Conclusion

- Biosorption of Cd(II) increases rapidly with increasing mass of adsorbent from 0.1 to 2.5 g with removal efficiency from 20 to 97 %, while maximum uptake 9mg/g was achieved at lower mass of adsorbent.
- The percentage removal of metal ion decreased with the decrease in pH .The optimum pH value is 6 to remove cadmium by biosorption process from polluted solution
- The metal concentration in aqueous solution decreases rapidly at the beginning of the experiment and remains nearly constant after 90 min. The increasing contact time increased the Cd(II) biosorption and it remained constant after reach equilibrium. The maximum percentage of Cd(II) removal was attained after about 100 min of shaking time.

- Hydroxyl (-OH), Carboxylic (C-O),aromatic compound and carboxylate (-COO-), carbonyl (-C=O) functional groups on the surface of rice husk play the major role in biosorption of Cd(II) ions by complex mechanism.
- Freundlich isotherm is the best fit model to describe the biosorption of Cd(II) onto rice husk with high correlation coefficient 0.983 and 1/n less than 1 .

Nomenclature

b	Langmuir constant , l/mg
B	constant to describe the energy of Interaction between the solute and the adsorbent surface.
C	Concentration in fluid, mg/l
C_o	Initial concentration, mg/l
C_t	Concentration at given time.mg/l
Cs	is the saturation concentration of solute (mg/l)
d_p	Particle diameter (m).
g	Gravitational force (= 9.81 m/s^2)
K_f	Liquid film mass transfer coefficient (m/s).
M	Mass of adsorbent (g).
n	Freundlich constant
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent (mg/g).
q_{max}	Adsorption equilibrium constant defined byLangumer equation (mg/g)
q_t	Amount of pollutant adsorbed at time t (mg/g)
Q	amount of solute adsorbed in forming acomplete mono- layer (mg/g).
R	Universal gas constant(=0.8314) (kJ/mol.K)
R_p	Radius particle, m
t	Time (s).
V	volume of solution (L).
w_o	Mass of adsorbent (kg).

Greek Symbol

μ_l	liquid viscosity (water $=1\times10^{-3}$Pa.s)
ρ_l	Density of liquid (kg/m^3)
ρ_p	Density of solid (kg/m^3)

List of Abbreviations

BET	BrunauerEmmetTeller method
FT-IR	Fourier Transform-Infrared Radiation
rpm	Revolution per minutes
WHO	World Health Organization

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Table 1 show the characteristic of rice husk

physical property	**%**
Particle size range (mm)	0.6 - 1
Equivalent diameter (mm)	0.775
Bulk density (g/ml)	0.2197
Solid density (g/ml)base dry	1.48
Surface area (m^2/g)	0.3018
Bed Porosity	0.911
Husk porosity	0.5
chemical composition	**%**
Volatile matter	64.7
Fixed carbon	15.7
Ash	19.6

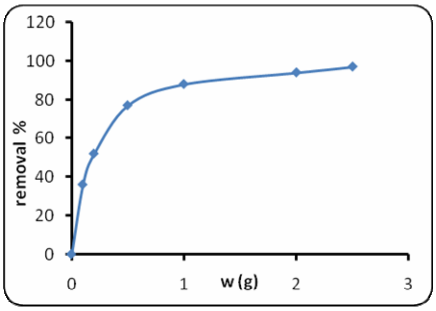

Fig. 1 Effect of different mass of adsorbent on Cd(II) removal efficiency, C_O=25mg/l, pH=6 , 150 rpm and t=3hr

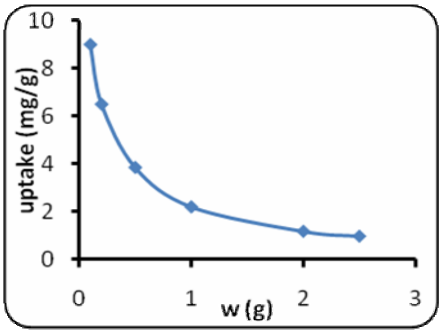

Fig. 2 Effect of different mass of adsorbent on Cd(II) up take, C_O=25mg/l, pH=6 150 rpm and t=3hr

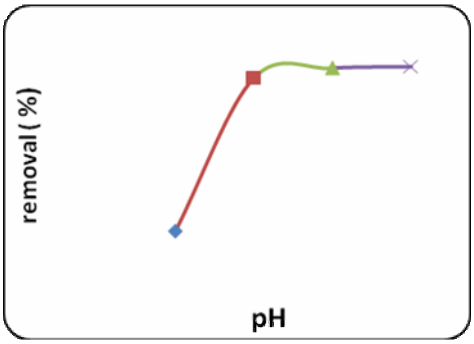

Fig. 3 Effect of different pH values on Cd(II) removal efficiency C_O=25mg/l , 2.5g of adsorbent, t=3hr and 150 rpm

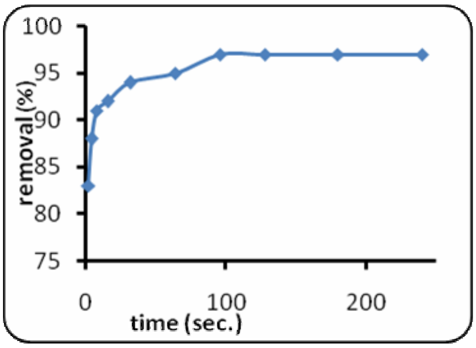

Fig. 4 Effect of different contact time on Cd(II) removal efficiency C_O=25mg/l, 2.5g of adsorbent, pH=6 and 150 rpm

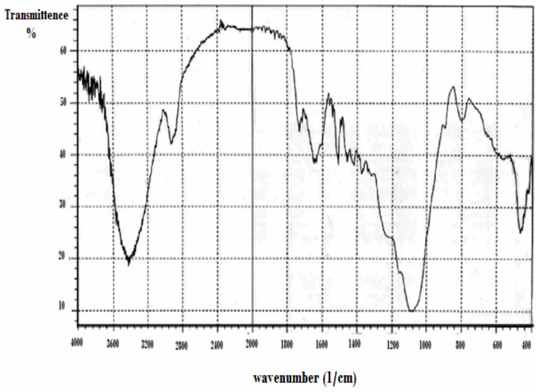

Fig. 5 FTIR spectra for rice husk biomass before loaded with 25 mg/l of Cd(II)

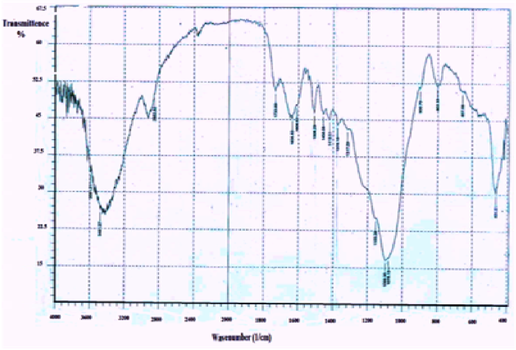

Fig. 6 FTIR spectra for rice husk biomass after loaded with 25 mg/l of Cd(II)

Table 2 Function groups before and after rice husk loaded with Cd(II)

FT-IR peak	Assignment groups	unloaded (cm^{-1})	loaded (cm^{-1})	Difference (cm^{-1})
1	Hydroxyl (OH)	3566.14	3591.21	25.07
2	Hydroxyl (OH)	3425.34	3481.27	55.93
3	Carbonyl (C=O)	1637.45	1635.52	1.93
4	Carbonyl (C=O)	1456.16	1458.08	1.92
5	Carboxylate (COO^-)	1373.22	1375.15	1.93
6	Carboxylate (COO^-)	1319.22	1317.29	1.93
7	Carboxylic acids and alcohols (C-O)	1157.21	1155.28	1.93
8	Carboxylic acids and alcohols (C-O)	1093.56	1099.35	5.79
9	Carboxylic acids and alcohols(C-O)	1074.28	1078.13	3.85
10	Aromatic compound	898.77	900.7	1.93
11	Aromatic compound	794.62	802.33	7.71
12	Aromatic compound	667.32	657.68	9.64
13	Aromatic compound	468.67	464.81	3.86
Total sum.		123.42		

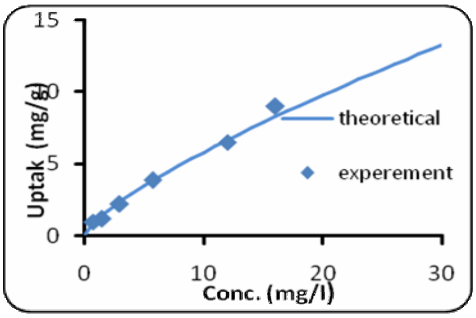

Fig. 7 The adsorption isotherm of Cd(II) onto rice husk biomas

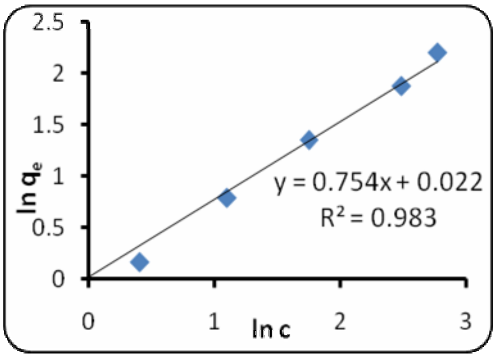

Fig. 8 Freundlich model (C=Conc. in mg/l and q_e= uptake in mg/g)

Table 3 Parameters isotherm for adsorption of Cd(II) ions onto rice husk

Model	Parameters	value	Refrence
Langmuir $q_e = \frac{q_{max} \times b \times C}{1 + b \times C}$	q_{max}(mg/l)	7.692	Langmuir (1918)
	b(l/mg)	0.1836	
	R^2	0.904	
Freundlich $q_e = K_f C^{1/n}$	K_f (l/g)	1.022	Freundlich (1907)
	n	1.326	
	R^2	0.983	
Temkin $q_e = \frac{RT}{b} \ln(K_T C)$	K_T(mg/g)	1.209	Temkin (1934)
	B=RT/b (l/mg)	2.53	
	R^2	0.880	
BET $q_e = \frac{BQC}{(C_s - C)[1 + (B-1)(C/C_s)]}$	B	9.9643	BET (1938)
	Q(mg/g)	3.5842	
	R^2	0.982	