Removal of Cadmium from Aqueous Solutions by Wheat Bran and Sunflower Shell

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Abstract

In this work two agricultural sorbents wheat bran and sunflower shell were examined to remove Cd(II) from synthetic solutions in a batch experimental setup. The effect of pH of the solution, initial concentration of metal ion and sorbent dose were investigated. (150 min) of adsorption time was found sufficient to reach equilibrium for cadmium ion on both adsorbents wheat bran and sunflower shell. The Freundlich, and Langmuir isotherm were employed and their isotherm constants were calculated at 25°C. Adsorption of metal ions, are pH dependent, and the results indicate that the optimum pH for the removal of Cd(II) was found to be 7.0 for both wheat bran and sunflower shell. The percentage of adsorption was found to be 95.7% and 94.9% on wheat bran and sunflower shell respectively at initial concentration of 50 mg/L and would be higher with higher initial concentration.

الخلاصة

في هذا العمل تم استخدام اثنين من المواد الزراعية وهي نخالة الحنطة وقشور بذور زهرة الشمس كمواد مازة لازالة ايون الكادميوم الثنائي من المحاليل المائية بنظام الدفعات التجريبية. تأثير حامضية المحلول, التركيز الاولي لايون المعدن وجرعة المادة المازة تم فحصها. 150 دقيقة من وقت الامتزاز وجد انه وقت كافي للوصول الى حالة التوازن لايون الكادميوم لكل من نخالة الحنطة وقشور بذور زهرة الشمس. تم تطبيق معادلتي Freundlich وLangmuir وحساب ثوابتهما عند درجة 25 درجة مئوية. امتزاز المعدن الثقيل يعتمد على معامل الحامضية واوضحت النتائج ان افضل قيمة لمعامل الحامضية في ازالة معدن الكادميوم هو 7.0 لكل من نخالة الحنطة وقشور بذور زهرة الشمس. وجدت النسبة المئوية للامتزاز بمقدار 95.7 و 94.9 لنخالة الحنطة وقشور بذور زهرة الشمس على التوالي عند تركيز اولي 50 ملغرام/ لتر وتزداد النسبة بزيادة التركيز الاولي.

Key words: Cadmium, adsorption, Wheat bran**,** equilibrium isotherm.

1-Introduction

The presence of heavy metals in the environment is a major concerns due to their toxicity for many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals will not degrade into harmless end products, therefore, the elimination of heavy metals from water and wastewater is important to protect public health (Abd-Al Hussein, 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. The main anthropogenic pathway through which cadmium enters environment is via wastes from industrial processes such as electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium-nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations and refining. (Wu J., *et. al.*, 2010)

From the analytical point of view, it is known that solid phase extraction (adsorption) is an effective technique based on the use of sorbent that retains analytes. The adsorption process, proved its advantage over the other processes because of its cost effectiveness and the high-quality of the treated effluent it produces. Activated carbon is widely used as an adsorbent due to its high adsorption capacity (Uzun and Guzel, 2000, Sudha *et al*, 2007).

Different cheap adsorbents are used or under investigations of these peat, marine algae, clays, maize cob, bagasse, palm fruit bunch, lalang leaf, saraca indica leaf and nile rose plant, which were used to remove dyes and metal ions from waste water(Ho Y S, and Mckay, 2000), (Abdel-Ghani and Elchaghaby, 2007). Beside that many chelating polymers have been used for this purpose (Jia *et al*, 2006), (Masram *et al*, 2007).

The cell wall of most agricultural waste contains natural polymers like cellulose, hemicellulose, pectins and lignin which are the most important sorption sites (Qaiser *et al* , 2007).

(Ozlem *et al*, 2001) investigated the adsorption of Fe(III) and Cu(II) ions from aqueous solutions on sunflower shell depending on pH, biowaste dosage and initial metal ion concentration. The sunflower shell showed single metal ion uptake 7.19 and 30.30 mg/gm for Fe(III) and Cu(II) respectively.

(Oualid and Mahdi, 2007) investigation on the removal of methylene blue from aqueous solutions by wheat bran is conducted in batch conditions. Removal kinetic data are determined, and the effects of different experimental parameters, such as wheat bran mass, initial concentration of methylene blue, agitation speed, solution pH, particle size, temperature, and ionic strength on the kinetics of methylene blue removal are investigated.

It can be safely concluded that wheat bran is much economical, effectual, viable, and can be an alternative to more costly adsorbents.

The aim of this work is to study the removal of cd(II) from aqueous solution by adsorption onto wheat bran and sunflower shell.. adsorption isotherm was determined and modelled by the Langmiur and Freundlich models. The influence of initial adsorbate concentration, adsorbent dosage and pH of the solution on adsorption process was investigated.

2-<u>Materials and methods</u>

2-1 Sorbent materials

Wheat bran is rich in proteins, carbohydrates, minerals and fats (A. Ozer, F. Tumen, 2003).The wheat bran was obtained from a market as solid waste and was used for sorption experiments without any treatment (Oualid and Mahdi, 2007). The wheat bran was sieved repeatedly, in order to eliminate wheat semolina, non-wheat bran solids, and fine particles of the material, and dried to constant weight. Finally, the sorbent material is screened to obtain a particle size in the range (0.3–1.25) mm and stored in a vacuum desiccator before use (Oualid and Mahdi, 2007).

Sunflower shell (dp<2500 μm) was soaked in 50% H_3Po_4 for 15 minutes and then thoroughly washed with deionised water. Treated sunflower shells was dried in oven at 110°C and kept for adsorption experiments (Özlem *et al*, 2001).

2-2 Synthetic solutions

The stock solutions (50 mg/L) was prepared in distilled water using cadmium nitrate salts, $Cd(NO_3)_4.4H_2O$. All working solutions were prepared by diluting the stock solution with distilled water so that the range of the initial metal ion concentration in the solution varied between (10, 20,30,40,50) ppm. The pH was adjusted using 0.1M NaOH and 0.1M Hcl solutions (A. et al, 2009).

2-3 Calibration curve (APHA Washinggton, D. C, 1985)

Table 1. Standard samples and absorbency for cadmium

الامتصاصية	تركيز النموذج القياسي (ppm)	ت
0.4361	0.01	1
0.9512	0.02	2
1.4745	0.04	3
1.9684	0.08	4
2.5191	0.16	5

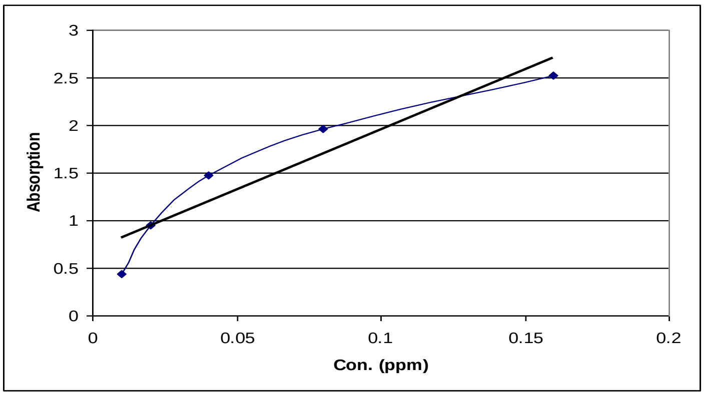

Fig.1: Calibration curve

2-4 Equilibrium isotherm

For isotherm studies, accurately weighted amount (6, 12, 24, 30) g/L of adsorbent (wheat bran or sunflower shell) were continuously stirred at 300 rpm with 100 mL of 50 mg/L metal ion. Agitation was provided at temperature of 25 °C for 150 min which is more than sufficient time to reach equilibrium. At the end of the equilibrium period the contents of the flasks were subsequently analyzed for residual concentration of metal ion. Percent removal (R%) was evaluated from the following equation 1:

$$R\% = \frac{Ci - Ce}{Ci} * 100 \quad \dots\dots\dots\dots\dots\dots(1)$$

The amount of metal ion adsorbed, q_e(mg/g) was obtained using Equation 2 (Wei *et al.*, 2009):

$$q_e = \frac{(C_o - C_e)V}{W} \quad \dots\dots\dots\dots\dots (2)$$

Where C_o and C_e are the initial and equilibrium concentration of metal ion (mg/L), respectively, V is the volume of solution (L) and W is the amount of adsorbent used(g).

2-5 Batch sorption experiments

Batch adsorption kinetic experiments were carried out by agitating at a speed of 300 rpm 12gm of adsorbent (wheat bran or sunflower shell) with 1 L aqueous solution of metal ion (cadmium) at a concentration of 50 mg/L in glass flasks placed on a shaker set, at constant temperature of 25 °C. The suspensions in all sorption assays were stirred for 150 min (Suantak et al, 2011) and then filtered through Wattman 42 filters to remove any suspended adsorbent. Final concentrations of metal were determined by atomic absorption spectroscopy (AAS).

The amount of metal ion adsorbed was determined from the difference between the metal ion concentrations in the initial and equilibrium states. The experiments were carried out in duplicate and the results are presented as mean values.

2-5-1 The effect of pH on sorption

This experiment was done with synthetic solutions in C=50 mg/L and different pHs of (3, 5, 7, and 9) for the two sorbents (Wheat bran and sunflower shell).

2-5-2 The effect of concentration on sorption

This sorption experiment was carried out with synthetic solutions at metal concentrations of (10, 20, 30, 40, and 50)mg/L in pH 5 for sorbent materials.

Sorption data for metal ion for two sorbents were fitted to the Langmuir and Freundlich isotherm models.

2-5-3 The effect of dosage of adsorbent on sorption

The effect of the wheat bran and sunflower shell dosage was studied in 50 mg/L metal ion concentration at pH value 5 and constant temperature 25 °C.

3-<u>Results and discussions</u>

3-1 Effect of pH on sorption

The effect of pH has been studied by plotting the curve between capacity adsorption of Cd (II) ion versus pH as shown in Fig. 2 and 3. The equilibrium data are given in Table 2. It was observed that capacity adsorption increased with pH of the liquid phase and reached an optimum value at pH 7.0. As the pH value became lower than 5, electrostatic repulsion between metal ion and H+ ion increased and low removal of Cd (II) ion was obtained. At the pH over 7.0 electrostatic repulsion decreased due to low positive charge density on the sorption sites and the metal adsorption process was enhanced.

Table 2. Equilibrium parameters for the adsorption of metal ion at different pH.
Temperature 25°C; Ci = 50 mg/L for cadmium ; dose of adsorbent 12 g/L

Name	pH			
	3	5	7	10
Wheat bran				
Ce mg/L	2.87	2.14	2.04	1.44
qe mg/g	0.35	0.41	0.45	0.47
Sunflower shell				
Ce mg/L	3.42	2.37	2.51	1.86
qe mg/g	0.38	0.39	0.39	0.4

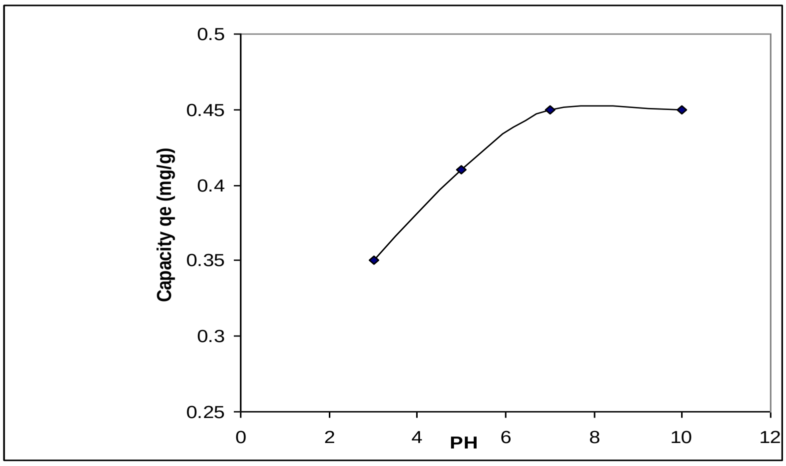

Fig. 2: Effect of pH on the biosorption of metal ion onto wheat bran biomass.

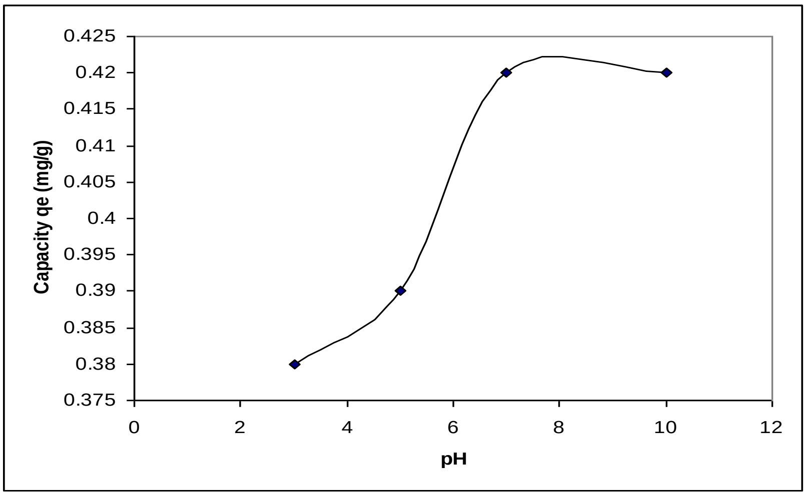

Fig. 3: Effect of pH on the biosorption of metal ion onto sunflower shell biomass.

3-2 Effect of initial concentration

The experimental results of adsorption metal ion at various initial concentrations (10, 20, 30, 40, 50 mg/L) for both adsorbent wheat bran and sunflower shell. The equilibrium data are given in Table 3. It reveals that, the actual amount of metal ion adsorbed per unit mass of adsorbent increased with increase in metal ion concentration. It means that the adsorption is highly dependent on initial concentration of metal ion. It is because of at lower concentration, the ratio of initial number of metal ion to the available surface area is low subsequently the fractional adsorption become independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the adsorption of metal ion is dependent upon initial concentration. The relation between the amount of metal ion adsorbed on the adsorbent surface (mg/gm) and the initial concentration of cadmium ion are shown in Fig 4 and 5.

Table 3. Equilibrium parameters for the adsorption of metal ion at different initial concentration.

Temperature 25°C; pH=5 ; dose of adsorbent 12 g/L

Name	Initial concentration (mg/L)				
	10	20	30	40	50
Wheat bran					
Ce mg/L	0.48	0.87	1.17	1.58	2.14
qe mg/g	0.08	0.16	0.27	0 .35	0.39
Sunflower shell					
Ce mg/L	0.92	1.2	1.36	1.71	2.52
qe mg/g	0.075	0.16	0.29	0.36	0.39

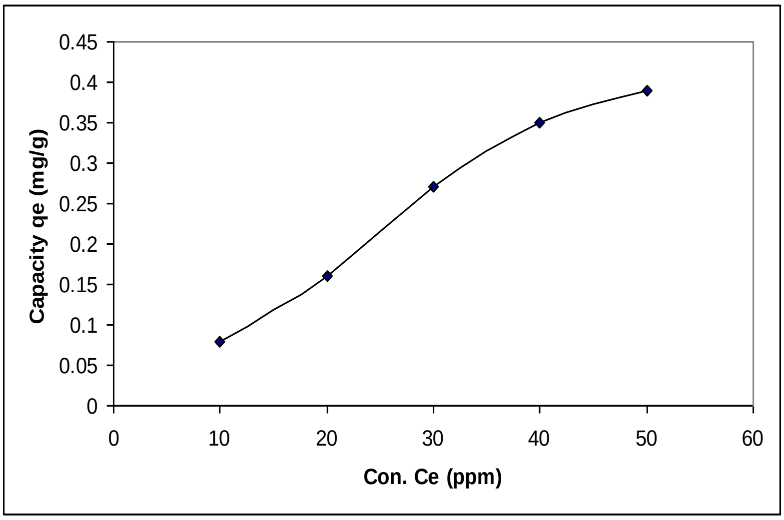

Fig. 4: Effect of initial concentration on the biosorption of metal ion onto wheat bran biomass.

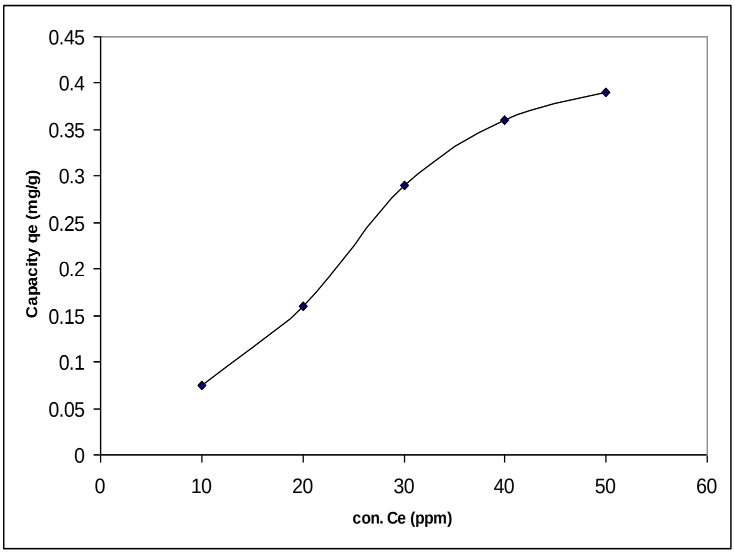

Fig. 5: Effect of initial concentration on the biosorption of metal ion onto sunflower shell biomass.

3-3 Effect of adsorbent dose

The effect of sorbent dosage on the uptake of Cd (II) was represented in Fig 6 and 7 which shows that sorption efficiency increased as the dose of sorbate increases for both wheat bran and sunflower shell. Because of at higher dosage more pores and surface were available at higher doses. The equilibrium data are given in Table 4.

Table 4. Equilibrium parameters for the adsorption of metal ion at different initial concentration.

Temperature 25°C; Ci = 50 mg/L for cadmium ; pH=5

Name	Adsorbent dose (g/L)			
	6	12	24	30
Wheat bran				
Ce mg/L	2.4	2.14	2.08	1.83
qe mg/g	0.16	0.19	0.39	0.79
Sunflower shell				
Ce mg/L	2.81	2.52	2.37	2.15
qe mg/g	0.16	0.19	0.47	0.79

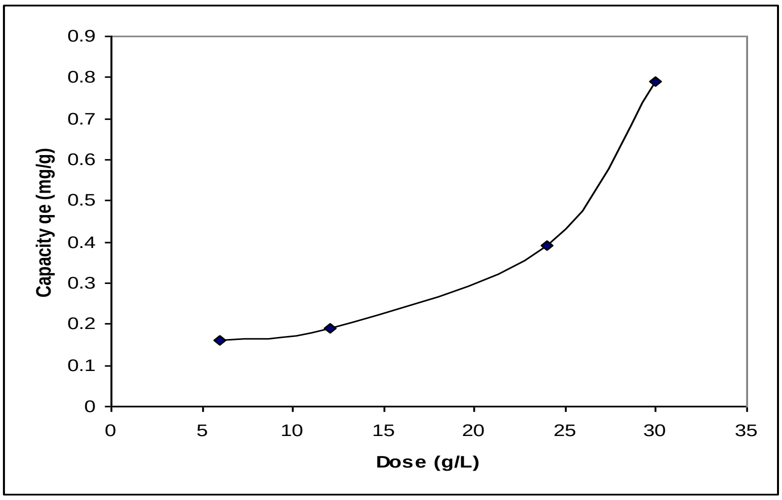

Fig. 6: Effect of dosage on the biosorption of metal ions onto wheat bran biomass.

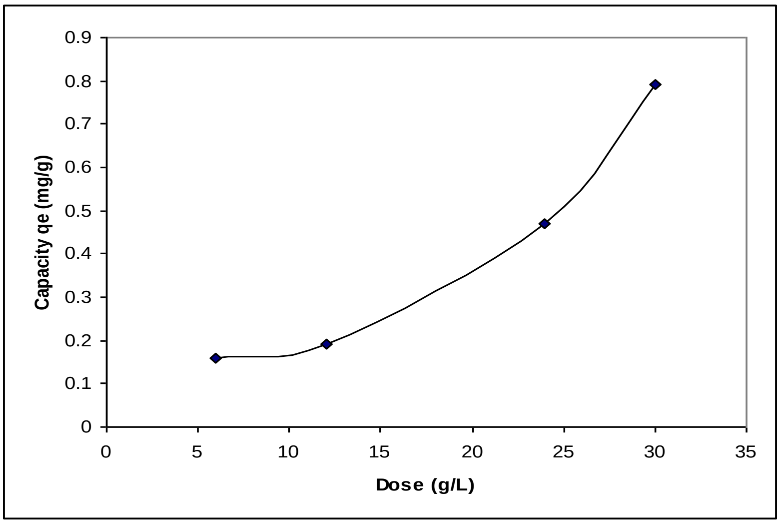

Fig. 7: Effect of dosage on the biosorption of metal ions onto sunflower shell biomass.

3-4 Adsorption isotherm

The equilibrium data of Cd (II) ion was fitted to the Langmiur and Freundlich isotherm models. These isotherms are expressed by the following equations

$$q_e = \frac{q_m k_a c_e}{1 + k_a c_e} \qquad \text{……………………..(3)}$$

$$q_e = k_f c_e^{1/n} \qquad \text{……………………..(4)}$$

Where *qe* is the amount of metal-ion adsorbed (mg/gm), *qm* is *qe* for a complete monolayer (mg/gm), *ka* is sorption equilibrium constant (L/g), *kf* and *n* are isotherm constants.

Eq. (3) and (4) are frequently used in the linear form after rearrangement. The experimental data for metal ion was also correlated by both linearised Langmiur and Freundlich equations (Eq.3 and 4). For metal ion the Langmuir and Freundlich isotherm constant are summarized in Table 1 for both wheat bran and sunflower shell.

Table 5:Isotherm constants for Cd(II) adsorption on the wheat bran and sunflower shell

	Wheat bran	**sunflower shell**
Freundlich		
Kf (mg/g)(L/mg)	0.04	0.014
1/n	5.82	6.07
r^2	0.83	0.95
Langmuir		
qm (mg/g)	-0.64	-0.62
ka (L/mg)	-0.39	-0.33
r^2	0.96	0.89

The Freundlich and Langmuir isotherms are compared to each other for wheat bran experiment and are given in Fig 8. The Freundlich and Langmuir isotherm plot for qe versus Ce for sunflower shell is shown in Fig 9. When the coefficient of determination (r^2) is used as a criterion for this study (Table 5), the data of Cd(II) ion are better fitted to the Langmuir isotherm with wheat bran. Cd(II) ion adsorption isotherm also agreed with the Freundlich model with sunflower shell (r^2=0.95) and the Langmuir isotherm model with sunflower shell (r^2=0..89). However, the general trend observed in adsorption profiles in Fig 8 and 9 revealed that the adsorption data were interpreted with both isotherms. The maximum adsorption capacities of Cd(II) ion per gram of wheat bran were calculated from Langmuir and Freundlich isotherm as 9.36 mg/gm and 6.6 mg/gm, respectively. The maximum adsorption capacities of Cd(II) ion per gram of sunflower shell were calculated from Langmuir and Freundlich isotherms as 7.91 mg/gm and 8.2 mg/gm respectively.

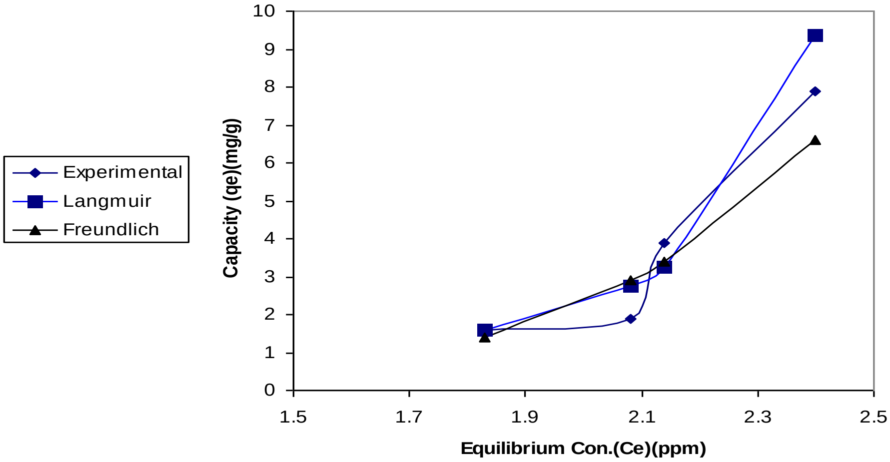

Fig 8: Isotherm of Cd(II) ion on wheat bran

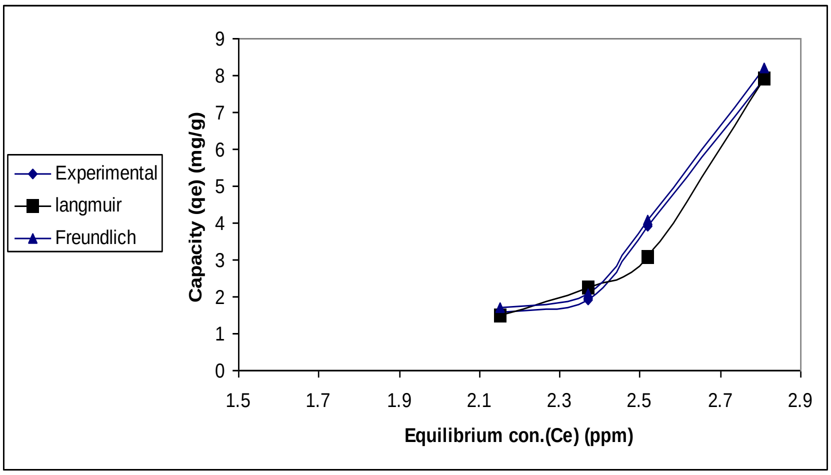

Fig 9: Isotherm of Cd(II) ion on sunflower shell

4-Conclusions

Agricultural by- product materials or modified natural polymers appear as effective and cheap sorbents for removal of Cd(II) from aqueous solution. Moreover, the materials could also be used for purification of water. The removal of metal ion from effluents is important to many countries of the world both environmentally and for water re-use. Wheat bran and sunflower shell have a very low economical value, can be an effective adsorbents for Cd(II) ion removal from aqueous system for environmental cleaning purposes.

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