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## REMOVAL OF CADMIUM FROM SYNTHETIC WATER BY USING AGRICULTURAL WASTES

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**ABSTRACT:** Heavy metals are among the most toxic contaminants of surface water. The main sources of toxic metals are industrial wastes from processes such as electroplating, metal finishing, chemical manufacturing, and nuclear fuel processing. Since most of heavy metals are non degradable into nontoxic metals end products, these concentration must be reduced to acceptable levels before discharged them into environment. The goal of this research Examine the ability of different media to reduce the concentration of cadmium ions in aqueous solution. The application of low-cost adsorbents obtained from plant wastes as a replacement for costly conventional methods of removing cadmium ions from waste water has been reviewed. Langmuir and Freundlich adsorption isotherms were applicable to the absorption process and their constants were evaluated. The single component adsorption of heavy metal ions named Cadmium (II) onto powdered activated carbon (PAC), karab, rice husks and corncobs from water aqueous solution has been investigated in batch. The multiple correlations simulated the experimental data of the batch tests, and regression equations were found for (PAC), karab, rice husks and corncobs with correlation coefficient for each media: 0.984, 0.946, 0.951, 0.932, respectively. In batch tests the effects of pH of solution, dosage adsorbent, contact time, initial concentration, mixing (stirring) speed and particle size diameter were studied. The optimum values of pH of solution was 5.5, for dosage adsorbent was 1g sorbent/100ml of Cd(II), for contact time was 30min, for initial concentration was 125 mg/L and for mixing (stirring) speed was 100 rpm. In continuous fixed bed tests, the effects of flow rate, and bed height of Cd (II) uptake onto rice husks studied. Different flow rates were used (1,3,5,7) L/hr. Different bed height (10, 20 and 30) cm was used. The removal of Cd (II) increased as the bed height increased and decreased as the flow increased.

**KEYWORDS:** Cadmium, Adsorption, Isotherm

### INTRODUCTION

Cadmium is highly toxic non-essential metal which accumulates in the kidneys of mammals and can cause kidney dysfunction [Alloway and Ayres, 1997].

Cadmium may interfere with the metallothionein's ability to regulate zinc and copper concentrations in the body. Epidemiological studies have revealed that Cd<sup>2+</sup> may contribute to some forms of cancer in humans and low exposures may result in kidney damage [Terry and Stone, 2002]. Cadmium is widely distributed in the environment of Iraq as a result of the use of galvanizing, pigments, stabilizers, thermoplastics, batteries and alloys. Moreover, the absence of the direct control from environmental protection agencies on above industries has increased the size of this problem.

Cadmium is responsible for serious damage to the health of humans:

- The most severe from Cd (II) toxicity in humans is "itai- itai", a disease characterized by excruciating pain in the bone [Sulaymon, et al., 2010].
- The harmful effects of cadmium include a number of acute and chronic disorders, such as renal damage, emphysema, hypertension, and testicular atrophy [Tilaki, et al., 2004].

- Cadmium toxicity contributes to a large number of health conditions, including the major killer diseases such as heart disease, cancer and diabetes. Cadmium concentrates in the kidney, liver and various other organs and is considered more toxic than either lead or mercury. It is toxic at levels one tenth that of lead, mercury, aluminum, or nickel [Sayed, et al., 2010].

The term "biosorption" is used to describe metabolism independent binding of heavy metals and/or radionuclides to nonliving adsorbents. The discovery and development of biosorption phenomena provide a basis for a whole new technology aimed at removal of heavy metallic species from dilute solutions in the range of 1 to 100 mg/L [Chong and Volesky, 1995].

There are various methods to treat the metal contaminated effluent such as precipitation, reverse osmosis, ion exchange, coagulation, and adsorption. But the selection of the treatment methods differ with respect to costs, complexity and efficiency. Among these technologies adsorption is a user-friendly technique for the removal of heavy metal. This process-seems to be most versatile and effective method for removal of heavy metal if combined with

appropriate regeneration steps [Said, 2010]. The biosorption equilibrium and kinetic data are fitted using different models and process parameters were evaluated [Sayed, et al., 2010].

The term biosorption commonly refers to the passive binding of metal ions or radioactive elements by dead adsorbents. It has to be distinguished from bio-accumulation which is usually understood to be an active, metabolically mediated metal-accumulation process occurring specifically in living organisms [Volesky and Naja, 2005].

In the experimental works, the dissolved Cd (II) in aqueous solutions has been selected as the sorbate. The single component adsorption of heavy metal ions named Cadmium (II) onto powdered activated carbon (PAC), karab, rice husks and corncobs from water aqueous solution has been investigated in batch tests. The Langmuir model can be represented as:

$$q_e = \frac{q_{\max} b C_f}{1 + b C_f} \quad (1)$$

This classical model incorporates two easily interpretable constants:  $q_{\max}$ , which corresponds to the maximum achievable uptake by a system; and  $b$ , which is related to the affinity between the sorbate and sorbent. The Langmuir constant “ $q_{\max}$ ” is often used to compare the performance of biosorbents; while the other constant “ $b$ ” characterizes the initial slope of the isotherm. Thus, for a good biosorbent, a high  $q_{\max}$  and a steep initial isotherm slope (i.e., high  $b$ ) are generally desirable [Aksu, et al., 2002].

The Freundlich (Freundlich, 1926) model has been widely used for many years.

The Freundlich equation has the general form:

$$q_e = K_f C_e^{1/n} \quad (2)$$

where  $K_f$  and  $n$  are constants and  $n > 1$ .

The Freundlich equation is basically empirical, but is often useful as a means for data desorption [Graaham, 1959].

(Metcalf and Eddy, 2003), define Freundlich isotherm as follows:-

$$\frac{x}{m} = q_e = K_f C_e^{1/n} \quad (3)$$

where  $x/m$  = mass of adsorbate adsorbed per unit mass of adsorbent after equilibrium, mg adsorbate/g activated carbon

$K_f$  = Freundlich capacity factor, (mg adsorbate/g activated carbon) \* (L water/mg adsorbate)<sup>1/n</sup>

$1/n$  = Freundlich intensity parameter. Other terms are defined previously.

The constants in the Freundlich isotherm can be determined by plotting  $\log(x/m)$  versus  $\log C_e$  and making use of the linearized form of equation (2) rewritten as:

$$\log\left(\frac{x}{m}\right) = \log K_f + 1/n \log C_e \quad (4)$$

A breakthrough curve represents the effluent concentration history (i.e. effluent concentration versus time) along the course of the adsorption concentration operation. The height of MTZ varies with the flow rate. The removal efficiency is influenced by various factors such as temperature of

solution, pH of solution, sorbent dosage, mixing (stirring) speed, contact time, particle size of the sorbent and initial metal ion concentration. Sayed, et al. (2010) found the effect of pH change in the range 1 to 8 on the adsorption of Ni (II) and Cd (II) on rice straw. The removal of Ni (II) was about 28% at a pH 1 and its reached maximum value 47% at about pH 5. Further increase of pH leads to slight decrease in Ni (II) removal efficiency.

The removal percentage of Cd (II) showed a rapid increase from 25% to 76% when the pH increased from 1 to 6. Mapolelo and Torto (2004) proved that the biosorption capacity of  $Cd^{2+}$ ,  $Cr^{3+}$ ,  $Cr^{6+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$  is dependent on pH. For all metal ions they studied, the optimal pH values are all greater than 5. The optimal pH for Cd and Pb biosorption is 5.8, while for Cr (III) and Pb is 5.2. As the pH further increases, the biosorption capacity subsequently decreases. The objective of this research was to investigate the optimum conditions of cadmium adsorption.

## MATERIALS AND METHODS

Powdered activated carbon (supplied by BDH chemicals Ltd Poole England, charcoal animal) is used as an adsorbent in the present work. For the rice husks the chemical composition predominantly contains cellulose (32-47%), hemicellulose (19-27%) and lignin (5-24%) [Sayed et al., 2010]. While, the palm Karab was collected from Baghdad, Khastawi type. Corncobs are available in Iraq and it is in hand in winter. In this study the argue-wasted product has been identified for sorbent for removal of heavy metal ions in aqueous solutions.

### Preparation of the adsorbent

The adsorbent was collected from Baghdad. Then sun dried and washed with tap water then rinsed with distilled deionized water several times and thereafter dried temperature of 105°C in an oven for 24 hours. Following cut the adsorbent into small pieces by using a housing food processor and through a sieve No.40 (ASTM E 11).

This was done to remove any large particles and to obtain particles of size less than (0.425 mm). This fine adsorbent was used in the batch experiments described below. For preservation, it was kept in plastic bags to minimize its contact with humidity.

### Preparation the synthetic polluted water sample

1000 mg/L standard stock solution of Cd (II) was prepared from  $Cd(NO_3)_2 \cdot 4H_2O$ . The required amount of metal salt was dissolved into 1L of distilled water and stir.

### Determination of metal ion concentration

All experiments after filtration, the synthetic polluted aqueous solution and the samples resulted from each treatment were analyzed for the concentration of Cd (II) by atomic absorption spectro- photometer (AAS) for concentrations more than 0.1 ppm and the Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) instrument for concentrations less than 0.1 ppm. Samples were read three times and the mean values were computed.

### Equipment

The equipment used in this study are:

1. Housing grinder for grinding the agricultural wastes.
2. Oven for drying the agricultural wastes (model 05, cap 64L, made in England).
3. Glass wares (pipette, conical flasks, volumetric flasks, graduated cylinders and beakers).
4. Disposable Polyethylene bottles for samples.
5. Sieves No. 40, 14, 10, 8 (ASTM E11 Body 316L MESH S-STEEL/ RF, made in Germany).
6. Calibrated pH meter of type (HANNA instrument, pH 211 Microprocessor pH meter made in Portugal) is used with its standards solution (standards are of pH=4, and 7), to measure the pH of the samples.
7. Digital Balance 4 decimal degrees (Precisa xp 220A), made in Switzerland.
8. Qualitative filter paper, made in China.
9. Sedimentation Jar Test (Aztec Environmental Control LTD, made in Germany).
10. Atomic absorption spectro- photometer (GBC 933 plus, made in Australia).

The optimum masses of activated carbon, rice husk, karab and corncobs which were 1, 1.5, 2, 2.5 g, respectively, and the optimum pH of solutions which was 5.5, were used for Cd(II) in these experiments. These experiments were used to obtain the equilibrium isotherm curves for single metal ions by plotting the mass of solute adsorbed per mass of adsorbent,  $q_e$ , against the equilibrium concentration of the solution,  $C_e$ , and then to obtain the equilibrium isotherm parameters.

A volume of 100 ml of metal ion solution in different initial concentration of 25-125 mg/L was placed in five beakers containing the fixed mass of the sorbent. The beakers were then shaken at a constant speed of 100 rpm in a Jar Test through a at temperature  $25^\circ\text{C} \pm 1$  for 30. After shaking, the sorbent was separated by filtration through a filter paper 0.425 mm. The filtrate was analyzed for the remaining metal ion concentration by atomic absorption spectrophotometer AAS.

A small laboratory scale of fixed-beds absorber is constructed in Sanitary Engineering Laboratory/ Building & Construction Department / Technology University. A schematic representation of the experimental equipment is shown in Figure (1), where the flow direction is downward by gravity.

The major equipment used in this setup are:

1. Two polyvinylchloride (PVC) tanks: one for inlet and another for outlet, each of (30 liter) capacity.
2. Three glass columns of 3 cm internal diameter and 40 cm height, as shown in Figure (1).
3. Centrifugal pump (type, Marquees water pump, model MKP 60/1) of PVC propeller and case and with capacity 40 L/min with 0.5 hp, used to pump the solution to the feed tank.

The experimental procedure carried out was as follows:

- Preparing the metal ion solution with desired concentration in the feed tank.
- The adsorber column was filled with the rice husks for the desired bed depth.
- The solution was passed by gravity to the adsorber column at the desired flow rate.

- Samples were taken at certain periods of time (15 min).
- The concentration of the metal ion in each sample was measured using AAS.

The media (rice husks) was packed in the column to the desired depth, and fed to the column as slurry by mixing the media with distilled water in order to avoid the formation of air bubbles inside the media. Then, solution was placed in the inlet container, and the outflow was adjusted by the valves number 1 and 2, as shown in Figure (1). Synthetic polluted water was prepared, and its pH was adjusted to the desired value and then placed in the inlet container to flow through the column by gravity. Samples were collected every 15min from the outlet, and its  $\text{Cd}^{+2}$  ion concentration was measured by Atomic Absorption Spectrophotometer.

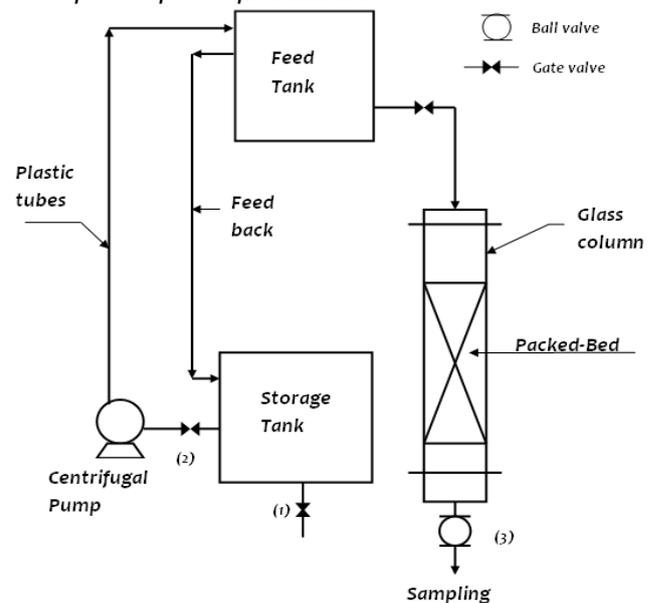


Figure (1): Schematic representation of the continuous flow system (column system) used in this study. (1) Drain valve; (2) Pump's section valve; (3) Sampling valve

## RESULTS AND DISCUSSION

In batch experiments, the influence of the dosage adsorbent, pH of solution, stirring speed and initial metal ion concentration on the removal of Cd(II), from solution by adsorption onto powder activated carbon, rice husks, karab and corncobs as an adsorbent was studied.

### Effect of pH solution

The removal of metal ions from aqueous solution by adsorption is related to the pH of solution. The first set of tests, therefore, examines the effect of pH on the effluent concentration.

The low biosorption capacity at pH values below 4.0 was attributed to hydrogen ions that compete with metal ions on the sorption sites. In other words, at lower pH, due to protonation of the binding sites resulting from a high concentration of protons, the negative charge intensity on the sites is reduced, resulting in the reduction or even inhibition of the binding of metal ions. Similar findings were reported by other researchers [Desi et al., 1998; Emani et al., 2003].

At high pH values, the removal takes place by adsorption as well as precipitation, due to formation

of metals hydroxide. This can be explained by the fact that, as the pH of the solution increased the OH ions in the solution increase and form some complexes with metal ions and precipitate as metals hydroxide [Al-Najar, 2009].

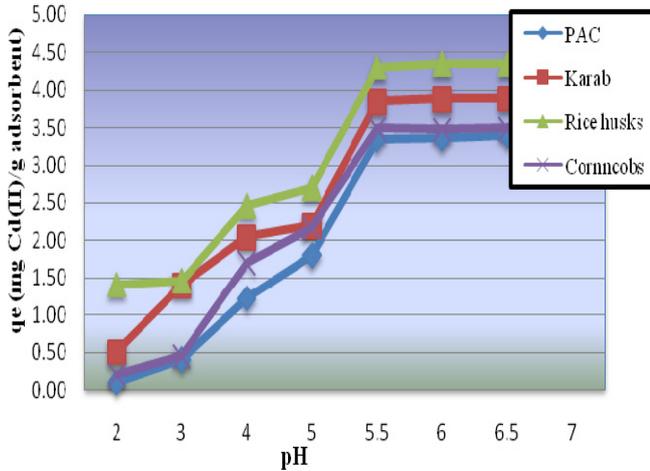


Figure (2):- Effect of pH on Cd(II) uptake for different materials

In general, it is noticed from the Figure (1) that the Cd(II) uptake of the three types of agro-adsorbents is very low at a pH of 2.0. Then, increasing the pH of the solution from 2 to 4 leads to a rapid increase in the Cd(II) uptake.

**The effect of dosage adsorbent**

The effect of dosage adsorbent on adsorption of Cd(II) at a constant adsorbate concentration was studied for the purpose of determining the optimum adsorbents dosage that will bring a best removal. First experiments (batch) started with a dose of 1 to 2.5 g of sorbent/ 100 ml cadmium solution of 50 ppm and a contact time of 30 min.

Results of experiments are shown in Figure (3). The metal percent removal increases with a further increase in the quantity of adsorbent the corresponding increase in the observed uptake of Cd(II).

Also, from Figure (3), the optimum sorbent amount required for efficient treatment can be well noticed. A crucial parameter for an optimal removal of metal ions in the wastewater.

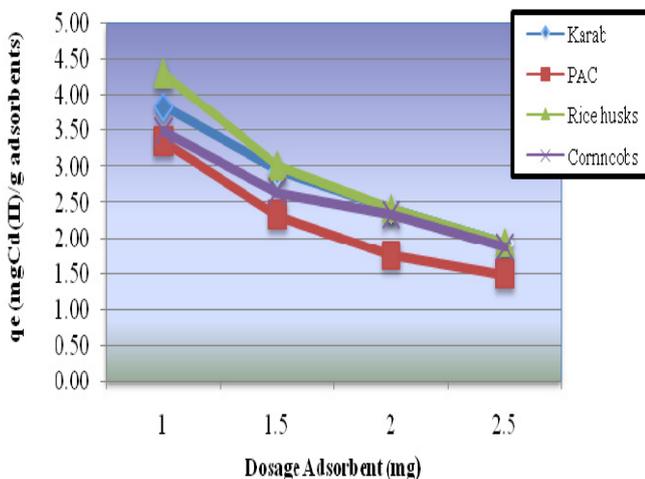


Figure (3):- Effect of dosage adsorbent on Cd(II) uptake for different materials

**The effect of contact time**

The kinetics of metal removal by rice straw was relatively fast within 5 min and during the first hour was remarkably changed with time. The equilibrium time was taken as 30 min for further experimental measurements, the results are shown in Figure (4).

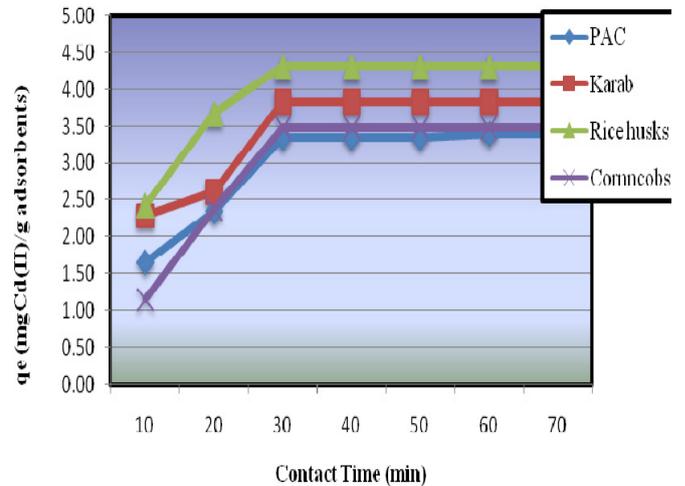


Figure (4):- Effect of contact time on Cd(II) uptake for different materials

**The effect of initial concentration**

The effect of initial metal ion concentration on the breakthrough curves for each metal ion was investigated for all the systems. The change in initial metal ion concentration will have a significant effect on the breakthrough curves.

Experiments were done at different initial concentrations of cadmium ion (25, 50, 75, 100 and 125 mg/L), and the other conditions were kept the same (pH=5.5, sorbent dosage=1g/100 ml, contact time= 30 min, stirring speed= 100 rpm, Vol. = 100 ml and particle size diameter= 0.425 mm) by rice husks, karab, corncobs and PAC.

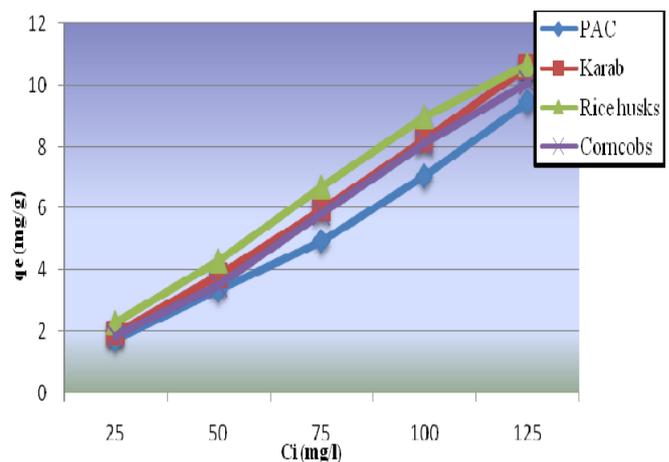


Figure (5):- Effect of initial concentration on Cd(II) uptake for different materials

Figure (5) shows a linear increasing relation between the adsorbents uptake and initial Cd(II) concentrations.

**The effect of stirring (mixing) speed**

The effect of stirring (mixing) the sorbent system on Cd(II) removal efficiency by different adsorbents was studied by varying the speed of mixing from 0 (with no-mixing as a control for comparison) to 200 rpm, while keeping the

dosage of sorbent, the contact time and optimum pH as constants. The Cd (II) uptake is increasing when the stirring speed is increasing from (0 to 100) rpm then remain constant for all adsorbents, as shown in Figure (6).

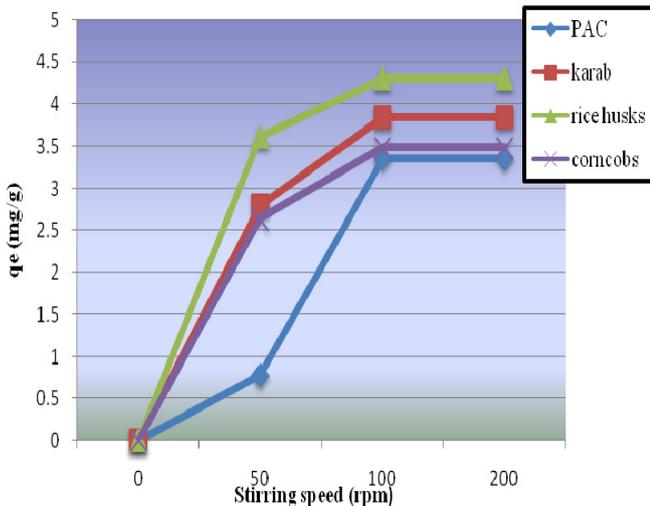


Figure (6):- Effect of stirring speed on Cd(II) uptake for different materials

**Effect of adsorbent particle size**

One can notice from Figure (7) the effect of adsorbents particle size on Cd(II) uptake is negligible and cannot be recognized easily. From Figure (7), these differences are meaningless compared with other influential factors (pH, dosage adsorbent, contact time, initial concentration and stirring (mixing) speed).

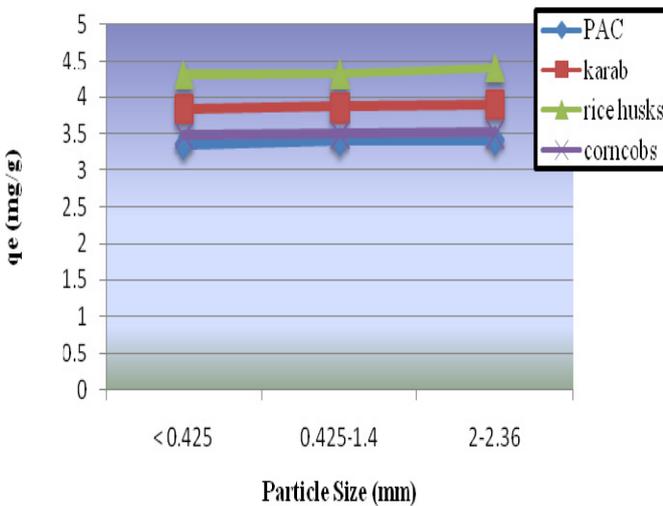


Figure (7):- Effect of particle size diameter on Cd(II) uptake for different materials

**EQUILIBRIUM ISOTHERM STUDIES**

**Langmuir model**

In batch tests, Figures (8), (9), (10) and (11) reveal the plot of  $C_f/q_e$  vs.  $C_f$  for rice husks, karab, corncobs and PAC, respectively. These Figures show a straight line which means that the equilibrium data is correlated well with Langmuir equations. The constants of Langmuir equation for each media were calculated from the slope and the intercept of the straight line and listed in Table (1).

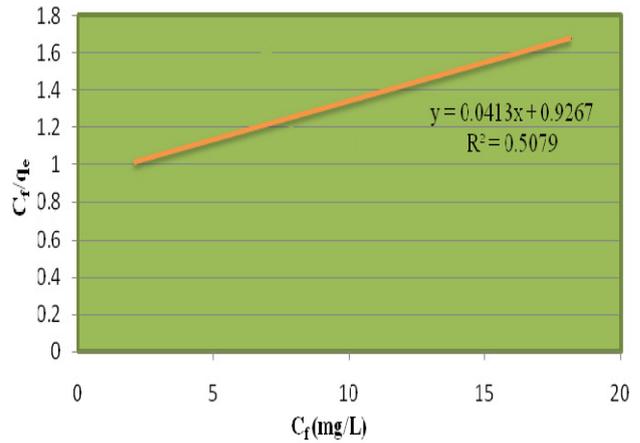


Figure (8):- Plot of  $C_f/q_e$  vs.  $C_f$  for determination of Langmuir constants for rice husks.

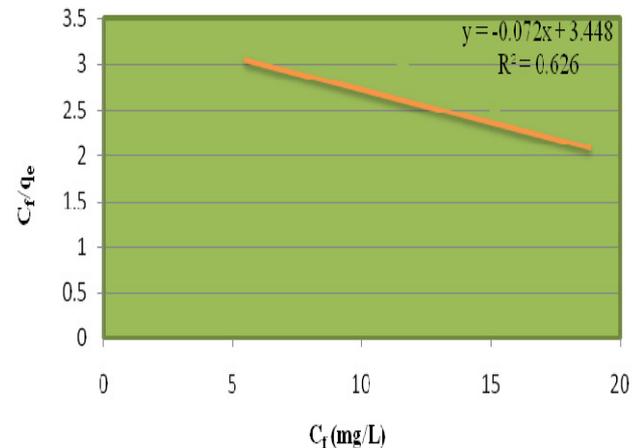


Figure (9):- Plot of  $C_f/q_e$  vs.  $C_f$  for determination of Langmuir constants for karab.

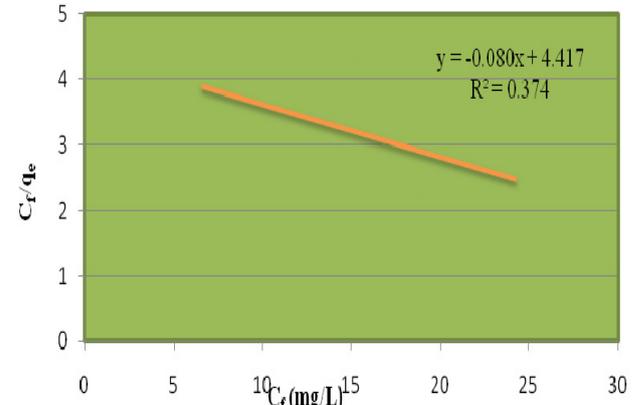


Figure (10):- Plot of  $C_f/q_e$  vs.  $C_f$  for determination of Langmuir constants for corncobs.

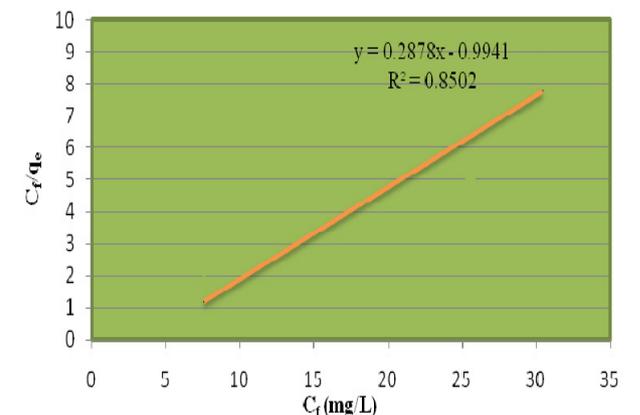


Figure (11):- Plot of  $C_f/q_e$  vs.  $C_f$  for determination of Langmuir constants for PAC

Table (1):-Constant values of Langmuir equation and the equation for each media.

Media	$q_{max}$	$b$	$R^2$	Equation
PAC	3.4843	0.994	0.85	$q_e=3.4843*0.994C_f/(1+0.994C_f)$
Karab	37.037	3.448	0.626	$q_e=37.037*3.448C_f/(1+3.448C_f)$
Rice husks	24.39	0.0413	0.508	$q_e=24.39*0.0413C_f/(1+0.0413C_f)$
Corncoobs	12.5	4.417	0.374	$q_e=12.5*0.4.417C_f/(1+4.417C_f)$

**Freundlich model**

Figures (12), (13), (14) and (15) illustrate the plotting of  $\text{Log } q_e$  vs.  $\text{Log } C_f$  for rice husks, karab, corncoobs and PAC, respectively. These Figures show a straight line (Freundlich adsorption isotherm) which means that the equilibrium data is correlated well with Freundlich equation.

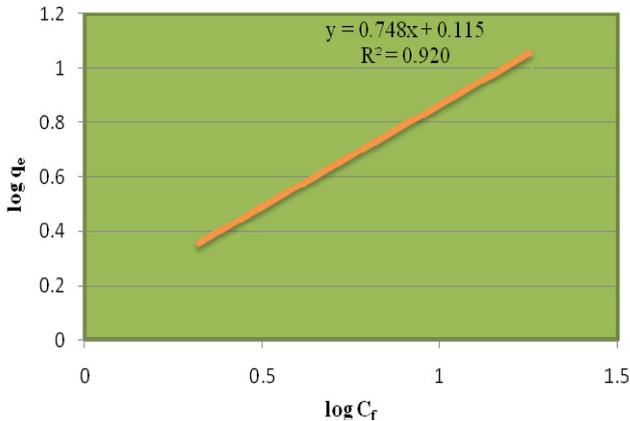


Figure (12):- Plot of  $\text{Log } q_e$  vs.  $\text{Log } C_f$  for determination of Freundlich constant for rice husks.

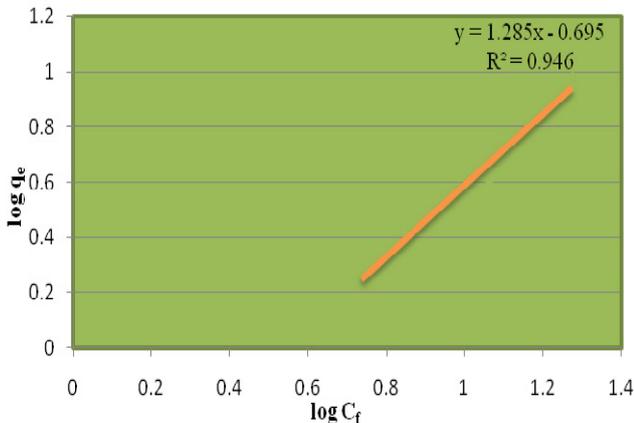


Figure (13):- Plot of  $\text{Log } q_e$  vs.  $\text{Log } C_f$  for determination of Freundlich constant for karab.

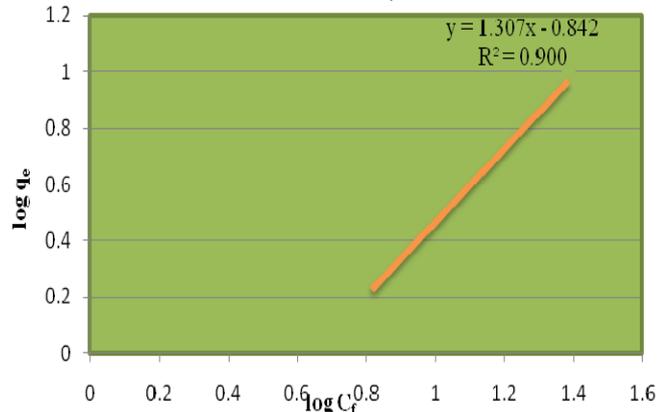


Figure (14):- Plot of  $\text{Log } q_e$  vs.  $\text{Log } C_f$  for determination of Freundlich constant for corncoobs.

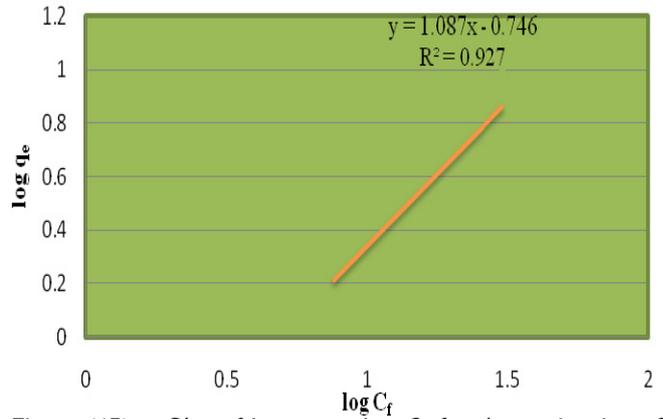


Figure (15):- Plot of  $\text{Log } q_e$  vs.  $\text{Log } C_f$  for determination of Freundlich constant for PAC.

The constants for Freundlich equation were calculated from the slope and intercept of the straight line, as tabulated in Table (2).

Table (2):- Constant values of Freundlich equation and the equation for each media.

Media	$K_f$	$1/n$	$R^2$	Equation
PAC	0.18	1.087	0.927	$q_e=0.18C_f^{1.087}$
Karab	0.202	1.285	0.946	$q_e=0.202C_f^{1.285}$
Rice husks	1.3	0.748	0.92	$q_e=1.3C_f^{0.748}$
Corncoobs	0.144	1.307	0.9	$q_e=0.144C_f^{1.307}$

**Multiple correlation**

The degree of relationship existing between three or more variables is called a multiple correlation. A regression equation is an equation for estimating a dependent variable, say  $X_1$ , from the independent variables  $X_1, X_2, X_3, \dots$  and is called a regression equation of  $X_1$  on  $X_2, X_3, \dots$ . In functional notation, this sometimes is written briefly as  $X_1 = F(X_2, X_3, \dots)$  read “ $X_1$  is a function of  $X_2, X_3$ , and so on” [Spiegel, 1979].

In batch experiments, the removal efficiency of Cd(II) (sorption process) affected by many factors, therefore, it can be simulated with the regression equation by application the Excel program. The Cd(II) uptake capacity has an optimum value for each factor. The optimum value for each factor was found and put in the equation to find the correlation coefficient of it. The effect of particle size diameter can be neglected, because there was no optimum value for Cd(II) uptake capacity. Table (3) shows the relationships between the Cd(II) uptake capacity and their affected factors with determination coefficient of the equation for each media.

Table (3):- The best equation for Cd(II) uptake capacity and its correlation coefficient for each media

Media	$R^2$	Equation
PAC	0.984	$y = 1.7 * 10^{-6} \frac{x_1^{3.05} x_3^{0.92} x_4^{1.22} x_5^{0.25}}{x_2^{0.58}}$
Karab	0.946	$y = 2.24 * 10^{-4} \frac{x_1^{1.72} x_3^{0.28} x_4^{1.16} x_5^{0.26}}{x_2^{0.54}}$
Rice husks	0.951	$y = 8.71 * 10^{-4} \frac{x_1^{1.16} x_3^{0.27} x_4^{1.07} x_5^{0.29}}{x_2^{0.72}}$
Corncoobs	0.932	$y = 1.59 * 10^{-5} \frac{x_1^{2.6} x_3^{0.52} x_4^{1.24} x_5^{0.23}}{x_2^{0.41}}$

Table (3):- The best equation for Cd(II) uptake capacity and its correlation coefficient for each media (continue)

Media	$Y_{practical}$ (mgCd (II)/g adsorbent)	$Y_{theoretical}$ (mgCd (II)/g adsorbent)
PAC	3.35	2.632
Karab	3.84	3.373
Rice husks	4.31	3.941
Corncoobs	3.49	2.892

Where:  $y$ : Cd (II) uptake capacity (mg Cd(II)/g adsorbent),  $X_1$ :pH,  $X_2$ : dosage adsorbent (mg),  $X_3$ : contact time (min),  $X_4$ : initial concentration (mg/L),  $X_5$ : stirring speed (rpm),  $y_{practical}$ : Cd (II) uptake capacity (mg Cd(II)/g adsorbent) calculated from batch tests and  $y_{theoretical}$ : Cd (II) uptake capacity (mg Cd(II)/g adsorbent) calculated from the equation by multiple correlation.

**Continuous tests**

In column tests, a series of experimental breakthrough curves were plotted for adsorption of a single component system. The experiments included studying the effect of flow rate (Q) and the effect of the height of the adsorbate bed (H).

**The effect of flow rate**

Four column experiments were carried out at different flow rates (influent) (1, 3, 5 and 7 L/h) and at constant initial conditions: pH 5.5, rice husks particle size (0.425-1.4 mm), bed height (20 cm) and initial cadmium concentration (100 ppm).

Data of effluent concentrations ( $C_f$ ) vs. time of these experiments were plotted in Figures (16) and (17). It is clear from these figures that as the flow rate increases, the time of breakthrough point decreases. This is because that the residence time of solute in the bed decreases as the flow rate increases and there is not enough time for adsorption equilibrium to be reached, which results in lower bed utilization, and the absorbent solution leaves the column before equilibrium.

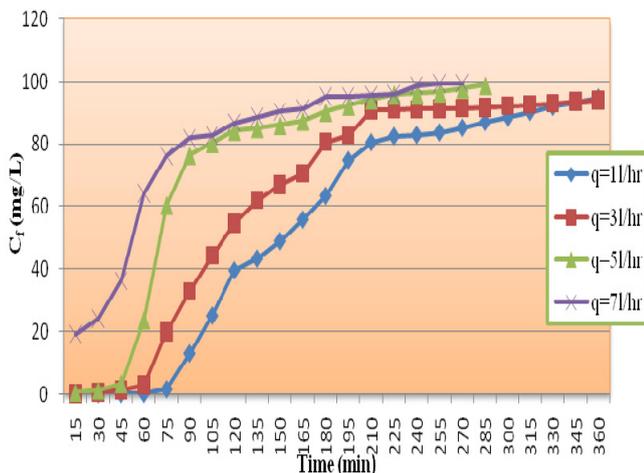


Figure (16):- Breakthrough curves of Cd(II) sorption for different flow rates

Figure (17) illustrates the effect of flow rate on the rate of uptake by plotting the accumulative Cd(II) uptakes ( $q_{ac}$ ) vs. time of column operation. From this figure, it can be seen that the accumulative uptake, at a certain time, increases when the flow rate increases, because the increase in flow rate means

more loading of metal ions onto the rice husks particles surfaces and then quicker saturation of rice husks adsorbent. The rate of Cd(II) uptake is clearly shown in the slopes of the linear portions of the relations in this figure.

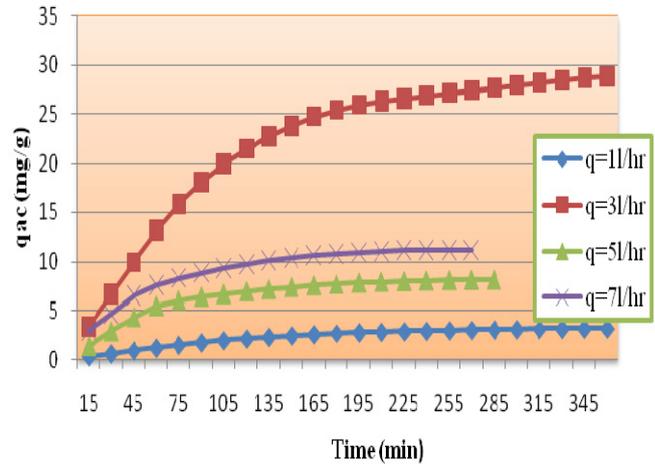


Figure (17):- Uptake curves for different flow rates

**The effect of bed height**

Rice husks bed height effect was examined by carrying out three experiments at different heights (H = 10, 20 and 30 cm) of weights (W = 56, 84 and 121 g), respectively. Other initial conditions were kept constants, flow rate (Q = 3 L/h), pH 5.5, particle size (0.425-1.4 mm) and average cadmium ion concentration ( $C_i = 100$  ppm).

Figure (18) shown that the time required to reach the equilibrium state increases as the bed height increases. This can be attributed to the presence of more available sites of the removal in the media when increasing the bed height and, therefore, the time required reaching the equilibrium state increases.

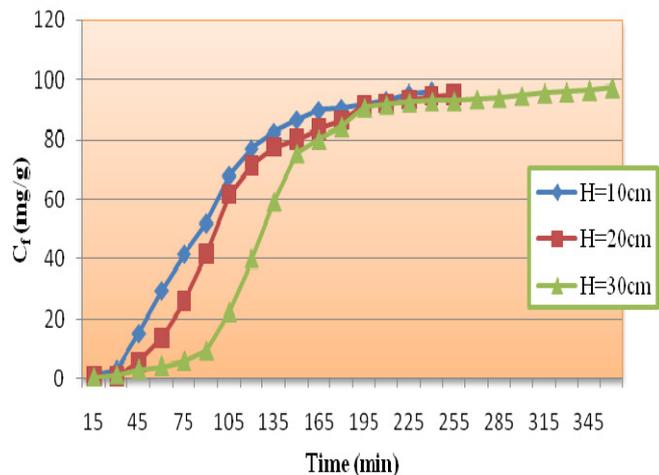


Figure (18):- Breakthrough curves of Cd(II) biosorption for different bed heights

Besides, the accumulative Cd(II) uptakes ( $q_{ac}$ ) for the rice husks vs. time of column operation were plotted as in Figure (18). From this figure, it can be seen that the time to saturation increases when the rice husks height increases, because using extra amount of rice husks results in extra surfaces for sorption, long flow paths and more contact time between the cadmium solution and rice husks particles.

**CONCLUSIONS**

Several sorption topics were studied and considered by this research and here below, the main conclusions that were obtained from batch tests and column tests:

□ For batch tests:

1. Rice husks, karab and corncobs are more effective to remove cadmium from synthetic waste water than activated carbon used in batch system.
2. Rice husks > karab > corncobs > PAC.
3. Optimum conditions for Cd (II) uptake capacity were pH of solution 5.5, for adsorbent dosage 1g adsorbent/100 ml of Cd (II), contact time 30min, initial concentration 125 mg/L and mixing (stirring) speed 100 rpm.
4. The Cd (II) uptake rate was not affected by particle size of adsorbents.
5. The equilibrium isotherm for the above systems is well represented by equations high correlation coefficient (0.927, 0.946, 0.92 and 0.9) for PAC, rice husks, karab and corncobs.
6. Rice husks can be used instead of activated carbon in wastewater treatment plant for the removal of Cd (II).
7. The multiple correlations simulated the experimental data in batch tests. The correlation coefficient for PAC, karab, rice husks and corncobs are: 0.984, 0.946, 0.951 and 0.932, respectively.

□ For continuous tests:

1. The breakpoint was related to the flow rate and the bed depth, i.e., the time required to reach breakpoint decreases with the increases of flow rate and decreases of bed depth.
2. The sorption results obtained from column tests are better than those of batch one for both effluent concentrations and uptake capacities. Besides, treatment by column is most practical.

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