Study of the Single and Binary Batch Systems to Remove Copper and Cadmium Ions from Aqueous Solutions using Dry Cabbage Leaves as Biosorbent Material

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The present study aims to remove Copper and Cadmium ions from aqueous solution using cabbage leaves as a low- cost biosorbent material in single and binary batch biosorption systems. The effect of pH solution, contact time, biosorbent dosage and initial metal ions concentration on the removal efficiency for two types of biosorption systems were examined. In the best conditions: the removal efficiency for Copper ions is greater than Cadmium ions for single and binary component systems. Equilibrium sorption data for two types of biosorption systems were fitted to the Freundlich, Langmuir and Redlich–Peterson isotherm models. The Langmuir model represents the equilibrium data better than the Freundlich and Redlich–Peterson models for two types of batch biosorption systems. The biosorption kinetics for the two metal ions followed the pseudo- second order kinetics indicating that the chemical sorption was the rate-limiting step.

Keywords: biosorption, heavy metals, equilibrium, isotherm, kinetics, cabbage leaves

As societies throughout the world are increasingly moving to greater levels of urbanization and industrial development, public concern is mounting over the state of the environment, and much attention is now being given to improving the environment for future generations [1]. Therefore, heavy metal pollution has become a major issue in many countries because their existence in drinking water and wastewater often exceeds the permissible standards [2].

Heavy metals such as lead, copper, cadmium and etc. are a sanitary and ecological threat. They are highly toxic and recalcitrant even at very low concentrations, and they can pollute drinking water resources [3, 4]. Heavy metals in human bodies tend to bioaccumulate, which may result in damaged or reduced mental and central nervous function, and damage to blood composition, lungs, kidneys and liver [5, 6].

Heavy metals are often derived from heavy industry such as electroplating and battery factories, metal finishing, and chemical manufacturing. Therefore, their removal from water and wastewater is important to protect public health [7, 8].

The removal of heavy metals ions from wastewater involves high cost techniques such as ion exchange, evaporation, precipitation, membrane separation etc. However, these common techniques are too expensive to treat low levels of heavy metals in wastewater [9, 10].

Biosorption is a new technology using in the recent years because the major advantage: economically and effectiveness in reducing the concentration of heavy metal ions to very low levels in an environment-friendly manner [11-14]. It's defined as the property of certain biomolecules to bind and concentrate selected ions or other molecules from aqueous solution [15]. Biosorbents fall under the

following categories: bacteria, fungi, algae, yeast, and industrial and agricultural wastes [16, 17].

A search for a low-cost and easily available adsorbent has led to the investigation of materials of agricultural and biological origin as potential metal sorbents [18]. Many materials which are cheap and readily available sources such as coal, coke, peat, wood, rice husk, or barley husk may be successfully employed for the removal of lead and other toxic heavy metals from aqueous solutions. The utilization of agricultural waste materials is increasingly becoming an important concern because these wastes represent unused resources and, in many cases, present serious disposal problems [19].

The aim present work is to study the feasibility of using dry cabbage leaves as a biosorbent for the removal of Cu(II) and Cd(II) ions from aqueous solutions. The main objectives of this work are: i) to study batch biosorption process in single, and binary systems, ii) to study the effect of *p*H solution, contact time, biosorbent dosage and initial metal concentrations on the removal efficiency, iii) to investigate the isotherm model that can describe the biosorption process, iv) to study the kinetics of metals biosorption to understand the mechanism of biosorption onto dry cabbage leaves.

Experimental part
Materials and methods
Chemicals

The stock solution (1000 mg/L) for Cu(II) and Cd(II) ions were prepared by dissolving appropriate amount of each metal salt in distilled water and then stored in glass containers at room temperature. The two metal salts were obtained from FLUKA Company. The desired concentrations were prepared by diluting the stock solution in accurate

proportions to different initial concentrations. The concentration of the metal was subsequently determined by using atomic absorption spectrophotometer (AAS), type: Atomic Absorption Spectrophotometer, (AAS), GBC 933 plus, Australia, the initial pH of the working solutions was adjusted to the required value by adding 0.1 M NaOH or HCl using a pH meter (WTW, inoLab 720, Germany).

Biosorbent Material

To remove dirt and impurities, the waste of cabbage leaves was washed with tap water then distilled water, dried at 100 °C for 3 days in the using electrical oven to remove the moisture content. The dried cabbage leaves milled and sieved to 0.5-3 mm and stored in plastic containers to ready for use.

The effects of pH, contact time, biosorbent dosage, and initial metal ion concentration on the removal efficiency of each metal were studied using classical approaches. In general, several stoppered conical flasks of 100 mL volume, each containing 0.5 g of biosorbent (except for dose effect) with 50 mL of 50 mg/L of each metal solution, were used. The suspension was shaken at 200 rpm for 120 min and temperature of 25°C using an incubator shaker and the residual amount of metal was determined after filtration using AAS. For the pH effect, the pH of the solutions was adjusted to 3, 4, 5, 6, 7 and 8. Solutions with pH above 6 were excluded owing to the precipitation of metals as hydroxide may occur. For the effect of contact time, the system was subjected to an agitation speed of 200 rpm, and the samples were collected from 10 to 150 min to be test for their metal remaining. The effect of biosorbent dose was studied in the range of 0.125 to 1 g. Different initial metal concentrations include 10, 25, 50, 75 and 100 mg/L were used to study the effect of metal concentration. After equilibrium, samples with (20 mL) were taken from the flask. These samples were filtered and the concentration of heavy metal ions in the solutions was determined by AAS. The percent of removal efficiency (R %) was calculated using equation (1).

$$R\% = \frac{C_o - C_e}{C_o} * 100 \qquad (1)$$

where: C_o and C_e are the initial and equilibrium sorbate concentrations in water (mg/L), respectively.

For binary systems, the same procedure of single system experimentation was followed, in which the mixture of equal amount of metal solution (50 mg/L) was subjected to biosorption process by using 0.5 g of dry cabbage leaves.

Isotherm experiments

The biosorption isotherm of Cu(II) and Cd(II) ions onto dry cabbage leaves were investigated by performing single and binary batch experiments. The experiments were conducted in 100 mL sealed conical flasks containing 50 mL of aqueous solution of each heavy metal (10–50 mg/L) and 0.5 g of dry cabbage leaves. The flasks were continuously shaken at room temperature (25 ± 3°C). The experiments were performed at the best pH values determined previously from the effect studies. Nine flasks were put in a shaker under a constant shaking speed (200 rpm) for 120 min. After biosorption, the sorbent was separated from the aqueous solution using a filter paper (WHATMAN, No. 42; diameter, 7 cm). The residual concentrations of Cu(II) and Cd(II) ions in single biosorption system were measured by AAS. The biosorption capacity at equilibrium conditions (q_e) was calculated using the following equation:

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

where: q_e is the equilibrium biosorption capacity (mg/g), C_o and C_e are the initial and equilibrium sorbate concentrations in water (mg/L), respectively, V is the volume of the sample solution and m is the mass of the used adsorbent (g).

The same procedure was repeated to measure residual concentrations of Cu(II) and Cd(II) ions in binary biosorption system.

Kinetic experiments

For kinetic experiments 50 mg/L concentration of Cu(II) and Cd(II) ion solutions were used. The sorption time varied between 0 and 150 min. In the isotherm experiments 0.5 g of dry cabbage leaves as a biosorbent was added in 50 mL of Cu(II) and Cd(II) ions solution. Samples of 4 mL were withdrawn and filtrated then the supernatant solutions were analyzed for the residual metal ion concentration by using AAS.

FTIR analysis

The infrared spectra of the dry cabbage leave particles before and after loaded by Cu(II) and Cd(II) were obtained using Fourier transform infrared spectroscope (Model: SHIMADZO, 800 series spectra- photometer). Normally, the spectra are measured within the range of 4000 – 1000 cm^{-1}.

Results and discussions
Effect of pH

Several previously reported studies indicated that pH of solution is the most important parameter effecting the biosorption capacity due to the variation in the pH value leading to differences in the surface properties of the sorbent and degree of ionization [20]. The removal efficiency of Cu(II) and Cd(II) in single and binary biosorption systems at 50 mg/L initial concentration for each heavy metal ions, 200 rpm agitation speed, 120 min contact time, 0.5 g/50 mL adsorbent dose, 1 mm particles diameter and 25 ºC temperature with pH ranging from 3 to 8 are studied and the results are depicted in figure (1). From this figure, it can be seen that the best pH value for two metal removals was around 6 for two biosorption systems. At lower pH, the active surface sites of the dry cabbage leaves were either positively charged, resulting the protons to compete with the metal ions, or dissociated, which results in a decrease in the metal removal efficiency. At a pH value higher than 6, the removal percentage decreased, it 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.
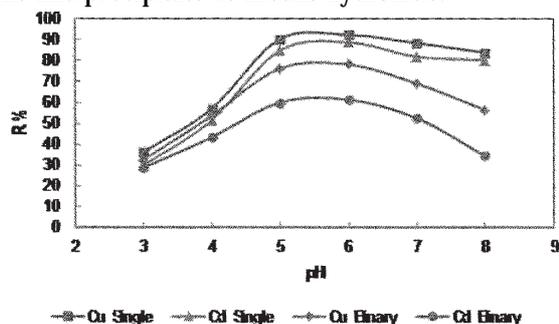

Fig. 1. Effect of pH on the single and binary biosorption systems of Cu(II) and Cd(II) ions onto cabbage leaves at C_o = 50 mg/L, agitation speed=200 rpm, contact time=120 min, adsorbent dose=0.5 g/50 mL, particles diameter=1 mm and temperature= 25ºC

Effect of contact time

The experiments were carried out at range of contact time between 10 and 150 min. Figure (2) shows the effect of contact time on the removal efficiency of each metal in single and binary biosorption systems. From this figure it can be seen that the Cu(II) and Cd(II) biosorption efficiency increased quickly within the first 45 and 75 min in a single and binary systems respectively. The equilibrium condition was approximately attained within 120 min contact time and then a relatively slow phase was observed beyond this time period. A further increase in contact time after 120 min had negligible effect on the removal efficiency. According to these results, the contact time was fixed at 120 min for the remaining of the two types of batch experiments to make sure that the equilibrium was achieved. The rate of metal removal is higher in the beginning due to a larger surface area of the biosorbent being available for the biosorption of the metals. After that the competitive among three metals ions on the available active sites has been intensive by these ions [21].
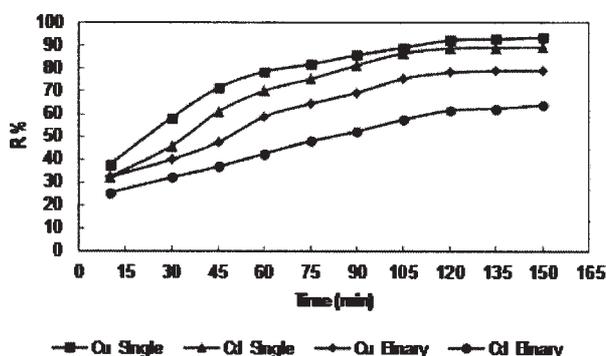

Fig.2. Effect of contact time on the single and binary biosorption systems of Cu(II) and Cd(II) ions onto cabbage leaves at best pH, C_o= 50 mg/L, adsorbent dose=0.5 g/50 mL, agitation speed=200 rpm, particles diameter= 1 mm and temperature= 25 °C.

Effect of Biosorbent Dosage

The biosorbent amount is also an important parameter to obtain the quantities uptake of metal ions. The effect of biosorbent dosage on the removal of metal ions was studied using dry cabbage leaves dosage of 0.125-1 g/ 50 mL at best operating conditions for single and binary systems as shown in figure 3. It was found that the retention of metals increased with increasing amount of sorbent dose up to 0.5 g / 50 mL of solution, this value was taken as the best amount for other trials. The results were expected because for a fixed initial metal concentration, increasing biosorbent amount provides greater surface area or biosorption site [22]. The removal efficiency of Cu(II) is higher than that of Cd(II) for single and binary systems. This may be due to the physical and chemical properties of Cu(II) to be more favorable to be adsorbed than Cd(II).

Effect of Initial Metal Concentration

The initial concentration of Cu(II) and Cd(II) ions provides between the aqueous and solid phases. Removal of these ions by 0.5 g dry cabbage leaves dosage was investigated by employing the metal ions solutions with (10, 25, 50, 75 and 100 mg/L) initial concentrations at 120 min contact time and pH 6, the results are depicted in figure (4). From this figure, it can be seen that the percentage removal of Cu(II) decreased from 93.1 to 54.93% and for Cd(II) 91.6 to 48.43% with increasing the initial metal ions concentrations from 10-100 mg/L in single biosorption system. Also its decreased from 84.63 to 40.45% and from 65.27 to 33.29%
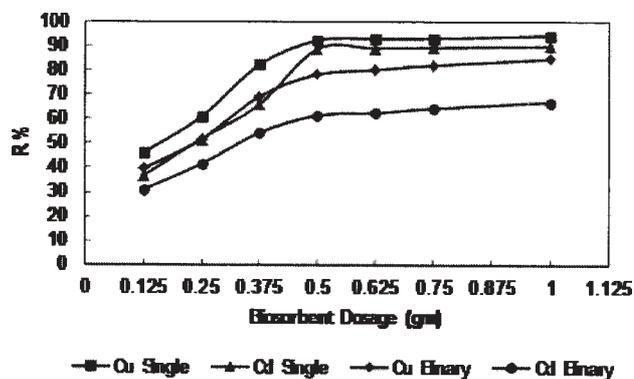

Fig.3. Effect of adsorbent dose on the single and binary biosorption systems of Cu(II) and Cd(II) ions onto cabbage leaves at best pH and contact time, adsorbent dose=0.5 g/50 mL, agitation speed=200 rpm, particles diameter= 1 mm and temperature= 25 °C
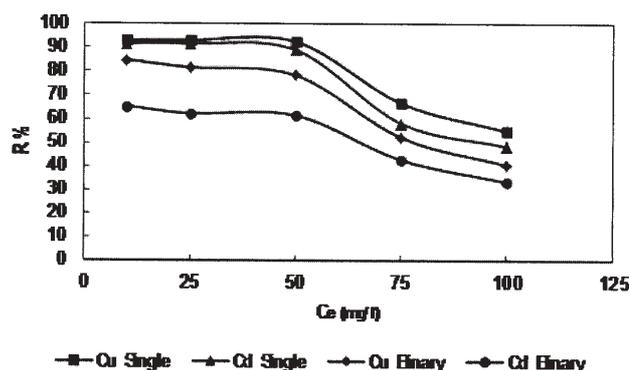

Fig. 4. Effect of initial concentration on the single and binary biosorption systems of Cu(II) and Cd(II) ions onto cabbage leaves at best pH, contact time and adsorbent dose, agitation speed=200 rpm, particles diameter= 1 mm and temperature= 25 °C.

for Cu(II) and Cd(II) respectively, with increasing the same initial metal ions concentrations in binary biosorption system. According to, [23], at lower metal ions concentration, the removal is higher due to larger surface area of sorbent available for sorption. When the concentration of metal ions is high, the percentage removal decrease since the available sites for sorption becomes less due to saturation of sorption sites. The same results were noticed by SEZEN et all. [24].

Biosorption Isotherm

Biosorption behaviors of metal ions in single and binary systems have been studied using the initial concentrations (10, 25, 50, 75 and 100 mg/L) for each metal ion. The Experimental biosorption capacity for Cu(II) is greater than Cd(II) in single and binary systems. This behavior may be attributed to several reasons from which the hydrated ionic radius as well as the electronegativity of Cu(II) and Cd(II) [25]. To find out the suitable isotherm models, analysis of isotherm data by adapting to different isotherm models is an important step that can be used for design purposes. In this study, the experimental isotherm data for the single biosorption system were fitted with the three well-known sorption isotherm models, namely, Freundlich, Langmuir and Redlich-Peterson isotherm models. Extended Freundlich, Extended Langmuir and Redlich-Peterson isotherm models were applied on the experimental data of binary biosorption system. All these previous models are presented in table 1.

The parameters for each model obtained from non-linear statistical fit of the equation to the experimental data (Statistica-v6). The data in table 2 shows that Langmuir and extended Langmuir isotherm models described the adsorption data for single and binary systems, respectively, it's better than other models depending on the value of

correlation coefficients. Experimental data and experimental isotherm data using Langmuir and extended Langmuir isotherm models for adsorption of Cu(II) and Cd(II) ions onto dry cabbage leaves in the single and binary biosorption system,
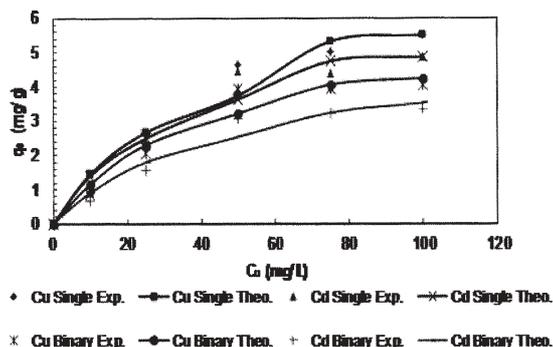

Fig. 5. Experimental data and experimental isotherm data using Langmuir and extended Langmuir isotherm models for adsorption of Cu(II) and Cd(II) ions onto dry cabbage leaves in the single and binary biosorption system, respectively

Isotherm Model	Non- Liner Equation	Eq. No.	Reference
Freundlich	$q_e = K_f C_e^{1/n}$	(3)	[26]
Langmuir	$q_e = \dfrac{q_m b C_e}{1 + b C_e}$	(4)	[27]
Redlich-Peterson	$q_e = \dfrac{A_R C_e}{1 + B_R C_e^{m_R}}$	(5)	[28]
Extended Freundlich	$q_{e,i} = \dfrac{K_i C_{e,i}^{n_i + n_1}}{C_{e,i}^{n_1} + \sum_{j=1}^{N} K_j C_{e,j}^{n_j}}$	(6)	[29]
Extended Langmuir	$q_{e,i} = \dfrac{q_{m,i} b_i C_{e,i}}{1 + \sum_{k=1}^{N} b_k C_{e,k}}$	(7)	[30]
Redlich-Peterson	$q_{e,i} = \dfrac{K_{Ri}(b_{Ri}) C_{e,i}}{1 + \sum_{k=1}^{N} b_{R,k} (C_{e,k})^{m_{R,k}}}$	(8)	[31]

Where: q_e is the adsorbed metal ions (mg/g); C_e is metal ions concentration in the solution at equilibrium (mg /L); K_f (mg/g) (L/ mg)$^{1/n}$ and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively. q_e is the adsorbed metal ions (mg/ g); q_m is the maximum sorption capacity for monolayer coverage (mg/ g); b is the Langmuir constant related to the affinity of the binding site (L/ mg); and C_e is metal ions concentration in the solution at equilibrium (mg /L). A_R (mg/g. L/mg); B_R (L/mg)^{mR} and m_R are the model parameters. K_i (mg/g) (L/mg)$^{1/n}$ and n_i are derived from the corresponding individual Freundlich isotherm equation for the component i. $C_{e,i}$ is the equilibrium concentration of the component i in the multi-component solution; $q_{e,i}$ is the equilibrium uptake of the component i, $q_{m,i}$ and b_i are the single component Langmuir parameters for component i. K_{Ri} (mg/g); b_{Ri} (L/mg) and $m_{R,i}$ are the Redlich-Peterson single component parameter for component i.

Single			
Isotherm Model	Parameters	Cu(II)	Cd(II)
Freundlich equation (3)	K, (mg/g)(L/mg)$^{(1/n)}$	2.2389	2.0252
	n	4.0051	4.2827
	R^2	0.8632	0.8477
Langmuir equation (4)	q_m (mg/g)	5.7455	5.0657
	b (L/mg)	0.4893	0.4521
	R^2	0.9523	0.9481
Redlich–Peterson equation (5)	A_R (mg/g L/mg)	1.9459	1.4667
	B_R (L/mg)^{mR}	0.1531	0.1110
	m_R	1.2228	1.2591
	R^2	0.9301	0.9352
Binary			
Extended Freundlich equation (6)	K (mg/g) (L/mg)$^{1/n}$	1.4392	0.7271
	n	3.6270	2.5968
	R^2	0.8671	0.8972
Extended Langmuir equations (7)	q_m (mg/g)	4.5578	4.1694
	b (L/mg)	2.1311	0.5040
	R^2	0.9550	0.9564
Redlich-Peterson equation (9)	k_R (mg/g)	20.1535	60.9052
	b_R (L/mg)^{mR}	0.1678	0.0131
	m_R	1.3770	1.6377
	R^2	0.9248	0.9334

Model	Equation	Linear Expression	Eq. No.	Reference
Pseudo- first order kinetic models	$q_t = q_{eq}\left(1 - e^{-k_1 t}\right)$	$\ln(q_{eq} - q_t) = \ln q_{eq} - k_1 t$	(9)	[32]
pseudo- second order kinetic models	$q_t = \dfrac{k_2 q_{eq}^2 t}{1 + k_2 q_{eq} t}$	$\dfrac{t}{q_t} = \dfrac{1}{k_s q^2{}_{eq}} + \dfrac{t}{q_{eq}}$	(10)	[33]
Intra-particle Diffusion Model	$q_t = k_{id} t^{1/2} + C$	$q_t = k_{id} t^{1/2} + C$	(11)	[34]

Table 3
EQUATIONS FOR THE SORPTION KINETICS MODELS

Where: q_{eq} is the amount of metal sorbed at equilibrium (mg/g); q_t is the amount of metal sorbed at time t (mg/gm); k_1 is the observed rate constant of pseudo-first-order kinetic model (1/min). k_2 is the served rate constant of pseudo-second-order kinetic model (g/mg.min); K_{id} (mg/g min$^{1/2}$) is the rate constant of intra-particle diffusion; C is the value of intercept which gives an idea about the boundary layer thickness.

Model	Parameters	Cu(II)	Cd(II)
Pseudo-first-order Equation (9)	q_{eq} (mg/g)	3.6906	4.6987
	K_1(L/min)	0.0282	0.0306
	R^2	0.9852	0.9148
Pseudo-second-order Equation (10)	q_{eq} (mg/g)	5.3418	5.2826
	K_2 (g/mg.min)	0.0089	0.007
	R^2	0.999	0.9945
Intra-particle diffusion Equation (11)	C	1.4093	0.9792
	K_{id} (mg/g.min$^{0.5}$)	0.2927	0.3101
	R^2	0.929	0.9471

Table 4
KINETIC MODEL PARAMETERS FOR Cu(II) AND Cd(II) IONS ADSORPTION CABBAGE LEAVES

respectively were presented in figure 5.

Biosorption Kinetic

Pseudo- first order, pseudo- second order and Intra-particle diffusion kinetic models were used to test the experimental data. The original and linearized equations of three kinetic models were described in table 3.

When plots of $ln(q_{eq}-q_t)$ versus t for eq. (9): k_1 and q_{eq} were determined for the slopes and intercept while plots of t/qt versus t for eq. (10) were used to determine k_2 and q_{eq} values from the slope and intercept. The values of K_{id} and C were determined by slope and intercept when plotted q_{eq} and $t^{0.5}$ for eq. (11).

Table 4 is show that the values of correlation coefficient (R^2) indicate a better fit of pseudo- second- order model with the experimental data compared to pseudo- first- order and intra-particle diffusion models. The values of q_e calculated from the second order kinetic model agreed very well with the experimental values, and the regression coefficients are over 0.99. Therefore, the second-order model can be applied for Cu(II) and Cd(II) sorption process figure 6. The first- order kinetic model was used for reversible reaction with an equilibrium being established between liquid and solid phases. Whereas, the second order kinetic model assumed that the rate limiting step may be chemical sorption.

FTIR analyses

FTIR analysis of dry cabbage leaves have been carried out, in order to find out which functions are responsible for adsorption of Cu(II) and Cd(II) ions. Figures 7, 8 and 9 shows the spectra of raw material and these materials included ions respectively.
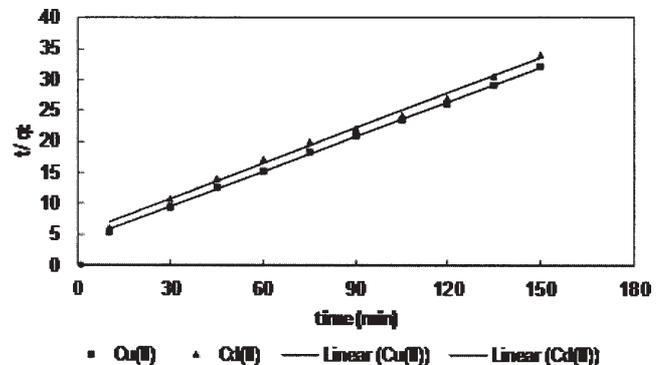
Fig. 6. Pseudo-second order kinetic model for batch biosorption of single component system for Cu(II) and Cd(II) ions onto dry cabbage leaves
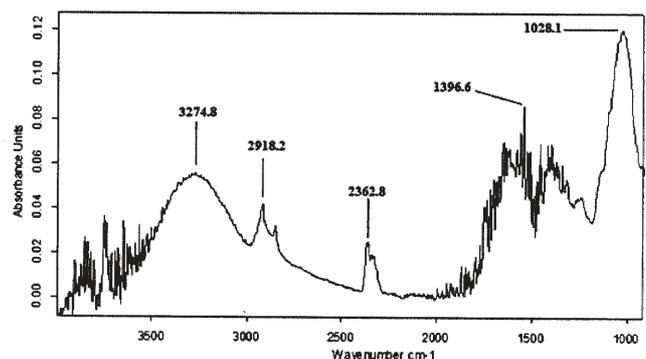
Fig. 7. FTIR analysis of dry cabbage leaves before loaded by heavy metals ion.
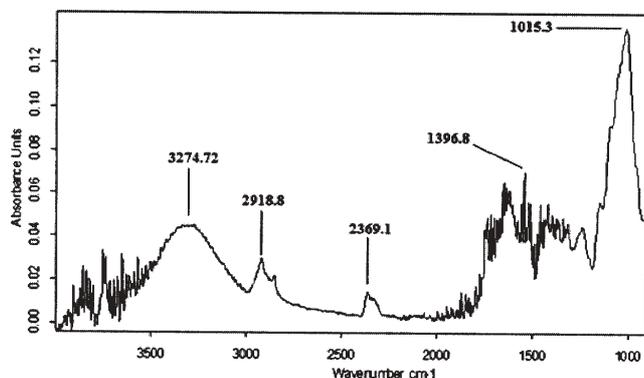
Fig. 8. FTIR analysis of dry cabbage leaves after loaded by Cu(II) ion

Fig. 9. FTIR analysis of dry cabbage leaves after loaded by Cd(II) ion

Bands displacement decreasing define the change in the structure with Cu(II) and Cd(II) imply the related functional groups to be responsible for the adsorption process. From these findings, it can be concluded that Cu(II) adsorbed more shifted than Cd(II). Figures 7, 8 and 9 show also that the bands of hydroxyl and carbonyl groups shifted to higher transmission (peaks of adsorption), and therefore it plays the major role in adsorption of these ions, according to the other studies [12-14].

Conclusions

This study confirmed that dry cabbage leaves is a promising biosorbent for copper and cadmium ions removal from aqueous solutions. The best condition for single and binary biosorption systems: $pH=6$, contact time= 120 min, biosorbent dose= 0.5 gm/50 mL of solution and initial concentration for each heavy metal ions was 50 mg/L. Maximum removal efficiency of Cu(II) and Cd(II) ions are 92.42% and 88.92% in single biosorption system, while 78.25% and 61.43% in binary biosorption system for two metals respectively at best conditions. The Langmuir and extended Langmuir isotherm models provides the best fit for the experimental isotherm data of the two metals for single and binary biosorption systems, respectively. In the single and binary systems: copper demonstrated the highest biosorption capacity while cadmium was the lowest owing to the competition condition. The pseudo-second-order kinetic model better explained the biosorption dynamics process for the two metals than the pseudo-first-order and Intra-particle diffusion kinetic model. From FTIR analysis it can be seen that the absorbance unit values were shifted to a new values due to biosorption of two heavy metal ions.

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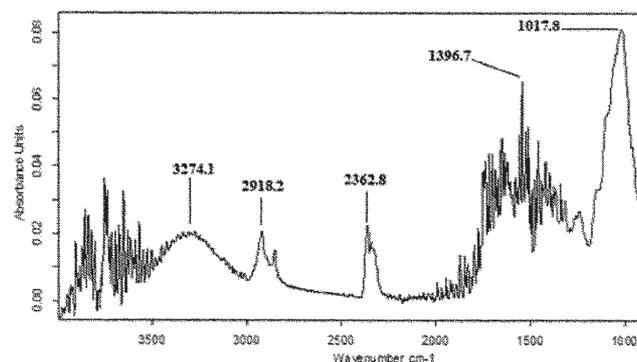8.YUN, Y. S. and VOLESKY, B., "Modelling of lithium interference in cadmium biosorption", Environ. Sci. Technol., 37, 2003, p. 3601.
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