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Competitive Adsorption of Cd (II) and Zn (II) in Single and Binary systems from Aqueous Solutions onto Cork Stopper Particles

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Abstract— The possibility of using cork stopper particles as a biosorbent for the removal of Cd (II) and Zn (II) from simulated wastewater was studied. Batch sorption experiments of single and binary components systems were conducted as a function of pH, sorbent dosage; contact time, and agitation speed were investigated to optimize the best conditions for maximum of metal ions removal. The experimental data fitted slightly best to the Langmuir isotherm model than to Freundlich and Temkin isotherm models. The experimental data proved that the adsorption kinetic of Cd (II) and Zn (II) could be described by a pseudo-first order model. The sequence for metal ions removal in single and binary system was Zn (II)> Cd (II), the removal efficiency of both metals decreased in the binary system.

Keywords— Heavy metals ions, Batchsorption, Kinetic models, Isotherm models, cork stopper particles.

1. Introduction

Water contaminated by heavy metals remains a serious environmental and public problem [6] Industrial wastewater often contains considerable amount of heavy metals and organic pollutants that would endanger public health and the environment if discharged without adequate treatment. The heavy metals are of special concern because they are non-degradable and therefore persistent[11], the most toxic metals are aluminum, chromium, magnesium, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead[19]. Cadmium and zinc are the heavy metals with a great potential hazard to humans and environment[20], they make their way to water bodies through wastewater from metal plating industries, industries of Cd–Ni batteries, phosphate fertilizer, mining, pigments, stabilizers and alloys [9].Poisoning of cadmium ions in humans causes high blood pressure, kidney damage and destruction of testicular tissue and red blood cells [3] In small amounts cadmium ions is associated with hypertensive diseases and considered as carcinogenic to men [6].Acute toxicity of zinc may result in sweet taste, throat dryness, cough, weakness, generalized aching, chills, fever, nausea and vomiting. Eating large amounts of zinc, even for a short time, can cause stomach cramps, nausea, and vomiting [16].Many chemical methods such as chemical precipitation [2], electro-flotation [7] ion-exchange [9] and reverse osmosis [3] have been used for the removal of heavy metals. However, these processes are economically non feasible especially in developing countries. The adsorption process has been found to be economically appealing for the removal of heavy metals with better removal efficiency from wastewater [10]. The optimization of adsorption methods should be carried out, first of all, by choosing or developing inexpensive adsorbents selective to the contaminants to be removed. Different types of biomasses (or adsorbents of natural origin) have been studied for the last two decades and adsorption characteristics of many of them have been widely investigated[5].There are many factors that affect the decision of choosing an adsorbent for removal of pollutants from water such as: economical factor (cost of the adsorbent), abundance, availability, and effectiveness of the adsorbent [17].Cork is the outer bark of the oak tree and it is industrially used for several purposes, principally the manufacturing of juice and wine stoppers[12][15][4]. Cork is known to be light, compressible and impermeable to liquids and gases, allowing its use in a lot of application fields. Some of them have been known for a long time, such as thermal and vibration insulation, wall and floor covering, or cork object making (cigarette box, desk pads, mouse pad, mats, shoe soles, memo board, shuttlecocks, .etc.). The main sector of cork industry remains the production of natural cork stoppers. The impermeability of cork to liquids and gases, derived from the fact that its closed cell walls are made up mainly of suberin, and its high compressibility and flexibility, make it ideal for sealing bottles [15].The use of natural, economic, and environmental friendly biosorbent to remove Cd (II) and Zn (II) in both single and binary systems was investigated in this work.

2. Materials and Methods

2.1 *Preparation of cork stopper particles*

The cork stopper particles used in this study was obtained from local markets. The collected biomaterial was extensively washed with tap water to remove soil and dust. Distilled water was used to wash the cork stoppers and after that dried in an oven (Type BBDE; S/N 20-601148, Korea) at 80°C for 10 hours. Dry biomass was cracked and grinded with house grinder .The product was sieved through a 1000 and 600 µm diameter mesh. The geometric mean diameter is given by $d_{gm} = (d_1 d_2)^{1/2}$ where d_1: is the diameter of lower sieve on which the particles are retained and d_2: is the diameter of the upper sieve through which the particles pass [3]. **Fig.1**shows the pictures of natural biosorbent (cork stoppers) that used in this study, (a) before and, (b) after grinded and sieved to 775 µm diameter.

(a) Beforegrinding (b) After grinding

Figure 1: A sample of natural and grinded cork stopper particles.

2.2 *Stock solution preparation*

A stock solutions of cadmium and zinc ions with concentration of (1000 mg/l) was prepared using cadmium and zinc sulfate crystals $CdSO_4$, $ZnSO_4$ respectively according to the equs(1,2):

$$M = C_1 \times V_1 \times \frac{M_{wt.\ of CdSO4}}{M_{wt.\ of Cd}} \quad (1)$$

$$M = C_2 \times V_2 \times \frac{M_{wt.\ of ZnSO4}}{M_{wt.\ of Zn}} \quad (2)$$

Where:

M: Mass of cadmium and zinc sulfate (mg).

C_1 ,C_2: Concentration of required cadmium and zinc (mg/l).

V_1,V_2: Volumes of solutions (l).

M_{wt} : Molecular weight (g/mole)

A (6.844 g,2.47g) of cadmium and zinc sulfates were dissolved in (1000 ml) of distilled water and the specific concentrations were measured using Atomic Absorption Spectrophotometer(Type, Shimadzu 7000, Japan) in the department of biological sciences/ University of Baghdad. The prepared solutions were kept at room temperature and used as stock solutions to prepare a (50mg/l) of both Cd (II) and Zn II).

2.3 *Experimental Work*

2.3.1 Effect of pH

About 100 ml of cadmium ions solution was placed in eight 250 ml volumetric flasks with 50mg/l concentration of Cd (II) solution. The initial pH of the solution was adjusted to a fixed value in the range of 2-7using 0.1M HCL and/or 0.1M NaOH. The pH of solution was measured prior to the addition of biosorbent. 0.5 g of biosorbent was added into the flasks, and then the flasks were placed in a thermostatic shaker (Type SI-600R, Korea) and agitated continuously for 120 minute and 200 rpm at room temperature. The pH, giving the maximum consequently, cadmium ions removal efficiency, was selected and utilized for the subsequent biosorption studies.The same steps and ranges were used for Zn (II).

2.3.2 Effect of contact time

The removal of Cd (II) and Zn (II) were also studied as a function of contact time at optimum pH. The rate at which biosorption takes place is an important factor when designing biosorptionsystem.it is necessary to establish the time dependence of metal removal for maximizing the rate of Cd(II) and Zn(II) uptakes by the biosorbent during equilibrium. Using eight 250ml volumetric flasks with; pH=(5.5-6),rpm=200,and W=0.5g, the time in which no further cadmium and zinc ions removal can be attained was considered as the optimum contact time.

2.3.3 Effect of agitation speed

The optimum agitation speed was investigated to maximize the contact time between metal ions and the biosorption site of biosorbent during equilibrium. To investigate the effect of agitation speed on the cadmium and zinc ions removal efficiency, four different agitation speeds of rotary shaker (100, 150, 200, and 250 rpm) were employed and the same procedure stated in section (2.3.1) was repeated with constant adsorbent mass, pH, and solute concentration. The agitation speed, giving the maximum cadmium and zinc ions removal efficiency's, was selected as the optimum for the subsequent biosorption studies.

2.3.4 Effect of biosorbent does

Seven volumetric flasks of 250 ml was used for both cadmium and zinc ions. The biosorbents were added in the range of 0.1-1g to 100 ml of the solution onto the flasks.

The flasks were then placed in a thermostatic shaker (Type SI-600R, Korea) and agitated continuously for (150-180) min, pH= (5.5-6), and 200 rpm. At the designated time, the two phases under investigation were separated using whatman filters No. 42 and the supernatant was collected for cadmium and zinc ions analysis using Atomic Absorption Spectrophotometer device. The mass of biosorbent dose, giving the maximum ions removal efficiency, was selected and utilized for the subsequent biosorption studies.

2.4 *Equilibrium isotherm*

The adsorption isotherm of Cd (II) and Zn (II) onto cork stopper particles was investigated in single and binary systems. The experiments were conducted in volumetric flasks containing a metal aqueous solution at initial concentration of 50 mg/l for each metal was used in conjunction with sorbent dosage (0.1-1g) at a constant speed 200 rpm for about 3h. The final concentration of the metal ion solution (Ce) at equilibrium was measured to calculate the adsorbed amount of metal ions at final equilibrium (qe) using Eq. (3):

$$q_e = \frac{V(C_o - C_e)}{m} \quad (3)$$

where qe =the equilibrium biosorption capacity (mg/g); Co and Ce= the initial and equilibrium adsorbate concentrations in water (mg/l), respectively; V= the volume of used solution (l); and m= the mass of used adsorbent (g).In single system the experimental data were fitted with three isotherm models, Langmuir Freundlich and Temkin models,while in binary system the data were fitted with tow models ,Extended Langmuir and Extended freundlich. These models are represented in **Table 1** and **Table 2**.

Table 1: single system Isotherms models

Model	Nonlinear form	Linear form	Plot	Ref
Langmuir	$q_e = \frac{q_m b C_e}{(1 + bC_e)}$	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b\,q_m} * \frac{1}{C_e}$	$\frac{Ce}{qe}$ VS Ce	[14]
	q_m is the maximum sorption capacity for monolayer coverage, (mg/g); b is the constant related to the affinity of the binding site, (L/mg).			
Freundlich	$q_e = KC_e^{1/n}$	$\ln q_e = \ln K + \frac{1}{n}\ln C_e$	Ln q_e VS $\ln C_e$	[15]
	Kisconstant indicative of the relative adsorption capacity of the adsorbent, $(mg/g)(L/mg)^{1/n}$; 1/n isconstantindicative of the intensity of the adsorption.			
Temkin	$q_e = \frac{RT}{b}\ln(K_T\,C_e)$	$q_e = B_1 \ln K_T + B_1 \ln C_e$	C_e VS LnC_e	[11]
	$B_1 = RT/b$; (R) is the universal constant (8.314 J/mol.K), b is the Temkin constant and T is the absolute temperature (K). (K_T) (l/mg) is the equilibrium binding constant corresponding to the maximum binding energy and the constant B_1 (KJ/mole) is related to the heat of adsorption.			

Table 2: binary system isotherm models

Models	Non Linear Form	Plots	Ref.
Extended Langmuir	$q_{e,i} = \frac{b_i q_{m,i} C_{e,i}}{\left(1 + \sum_{j=1}^{n} b_j C_{e,j}\right)}$	$\frac{Ce}{qe}$ vs Ce	[17]
	$q_{m,i}$ and b_i are the single component Langmuir parameters for component i.		
Extended Freundlich	$q_{e,i} = \frac{K_i C_{e,i}^{ni+n1}}{C_{e,i}^{n1} + \sum_{j=1}^{N} K_j C_{e,j}^{nj}}$	Ln q_e vs $\ln C_e$	[13]
	K_i and n_i are derived from the corresponding individual Freundlich isotherm equation for the component.		

2.5 *Fouriertransforminfrard analysis (FT-IR)*

The FT-IR spectra of cork stopper particles before and after cadmium and zinc ions biosorption was examined to identify the functional groups which are responsible for metals uptake and frequency changes of the functional groups in the biosorbent. In order to have a sample of cork stopper particles after ions biosorption on its surface, the following experiment was carried out: One gram of dry (cork stopper particles) was contacted with 100 ml of 50 mg/l of Cd (II) concentration in a flask. The cadmium ions solution was adjusted to pH value of 6. The sample was left on a shaker for 150min at agitation speed of 200rpm and then, the sample was filtered through Whatman No. 42 filter Paper. The supernatant was discarded and the biomass of cork stopper particles on filter paper was left to dry. Dried sample was collected and analyzed by FT-IR spectrophotometer (typeIRPRESTIGE-2; Shimadzu 8000, Japan) in the laboratory of organic chemistry / University of Al Nahrain. The same experiment with conditions of pH (5.5), rpm=200, and time = 180 min was applied with zinc ions in order to obtain the required sample.

2.6 *Kinetic experiments*

The external mass transfer (k_f) was obtained by using a well stirred batch contactor. In this step a known amount of adsorbent is stirred with a constant volume of solution. This solution was placed in 2 liters Pyrex beaker. A 2-bladed stainless steel axial flow impeller (Wiggen Hauser, Germany) was fixed at the center of the beaker. The experimental procedure was as follows: two beakers were used one of them was filled with 1.0 liter of Cd(II) solution of 50mg/l concentration and the other filled with 1.0 liter of Zn(II) solution of 50mg/l. The pH of the first solution was adjusted to 6 and the second solution was adjusted to pH 5.5. The agitation started before adding the biosorbent. At zero time, an accurate mass of biosorbent was added. The biosorbent suspensions were stirred for (150-180) min and samples were collected and filtered through a whatman filter No.42. The filtrates were analyzed using Atomic Absorption Spectrophotometer. The optimum speed was obtained by repeating the experiments for Cd(II) and Zn(II) with different agitation speeds (200, 400, 600 and 1000 rpm).The necessary dosages of dried biomass to reach an equilibrium concentrations of C/C_o= 0.05, (95% removal efficiency) were calculated from isotherm and balance equations as follow (in case of Langmiur model): [2]:

$$q_e = \frac{V_L(C_o - C_e)}{W_o} = \frac{q_m\, b\, C_e}{1 + b\, C_e} \quad (4)$$

$$W_O = \frac{V_L(C_o - C_e)(1 + b\, C_e)}{(q_m\, b\, C_e)} \quad (5)$$

2.6.1 Pseudo-firstorderkinetic model

The Pseudo-first order kinetic model was the first equation for the bisorption of liquid/solid systems based on solids capacity. It is widely used sorption for the sorption of solutes from liquid solutions and can be presented through the following[8]

$$\frac{dq_t}{dt} = K_L(q_{eq} - q_t) \quad (6)$$

Integrating linearize (6) with the conditions; t = 0 to t = t and q_t= 0 to q_t= q_t , gives:

$$ln(\frac{q_{eq}}{q_{eq} - q_t}) = K_L t \quad (7)$$

q_{eq} "the amount of adsorbat adsorbed at equilibrium (mg/g)"; q_t "the amount of adsorbat adsorbed at time t (mg/g)"; and K_L "the equilibrium rate constant of pseudo-first order sorption (min^{-1})". Equation (7) could rearrange to get a linear form:

$$ln(q_{eq} - q_t) = ln\, q_{eq} - (K_L\, t) \quad (8)$$

In order to fit equation (8), the equilibrium capacity ($q_{eq.}$) must be recognized to experimental data. The values of $\ln(q_{eq} - q_t)$ against t may be plotted from which k_L and q_{eq} represent the slope and intercept respectively.

2.6.2 Pseudo second order Model

The pseudo-second-order model assumes that the depleting of the site of adsorption is proportional to the square number of unused sites. There are several assumptions explained the pseudo-second order kinetic model [7].

- A monolayer of adsorbate is represented on the surface of adsorbent .
- The adsorption energy for each adsorbent is equally based on surface coverage .
- The adsorption takes place on sites and no interactions between adsorbents.

The equation may be represented as :

$$\frac{dq_t}{dt} = k_s\, (q_{eq} - q_t)^2 \quad (9)$$

k_s "the rate constant of adsorption (g/mg .min)", q_{eq} "the amount of pollutant adsorbed at equilibrium (mg/g)", q_t " amount of adsorbate on the surface of the adsorbent at any time t, (mg/g)".

Rearrangement of equation (9) gives:

$$\frac{dq_t}{(q_{eq} - q_t)2} = k_s dt \quad (10)$$

The boundary conditions were t= 0 to t = t and q_t= 0 to q_t= q_t ; the integrated form of equation (10) becomes:

$$\frac{1}{q_{eq}-q_t} = \frac{1}{q_{eq}} + k_s t \quad (11)$$

Which is the integrated rate law for a pseudo-second order reaction Equation (11) can be rearranged to obtain:

$$q_t = \frac{1}{\frac{1}{k_s q_{eq}^2} + \frac{t}{q_{eq}}} \quad (12)$$

Which has a linear form of

$$\frac{1}{q_t} = \frac{1}{k_s q_{eq}^2}\frac{1}{t} + \frac{1}{q_{eq}} \quad (13)$$

The values of 1/qt against 1/t plotted and the values of ks and qeq represent the slope and intercept of the plot, respectively.

2.6.3 Intra-particle diffusion model

It may be represented as[20]:

$$q_t = k_{id} t^{1/2} + C \quad (14)$$

Where: q_t (mg/g) "the adsorbed amount at time t (min)", K_{id} "the rate constant of intra-particle diffusion (mg/g $min^{1/2}$) ", C "(mg/g) the value of intercept which gives an idea about the boundary layer thickness", i.e. the larger intercept increased the boundary layer effects .

3. Result and discussion

3.1 *Effect of pH*

Different pH values ranged from 2 to 7 were used as shown in fig.2, which represents the relation between the removal efficiency of cadmium and zinc ions and different pH values of the solution. The Cd (II) removal was maximum of 80.96% at pH 6, while, the removal of Zn (II) reached 88.55% at pH of 5.5, and then there was a decreasing trend. Beyond the values of pH 6.0 and 5.5, Cd (II) and Zn (II) tend to precipitates due to hydroxide formation at high pH values and make the real sorption studies impossible[14], the pH 6 was taken as the optimum value in binary system. The result agrees with that obtained by [8] and [10].

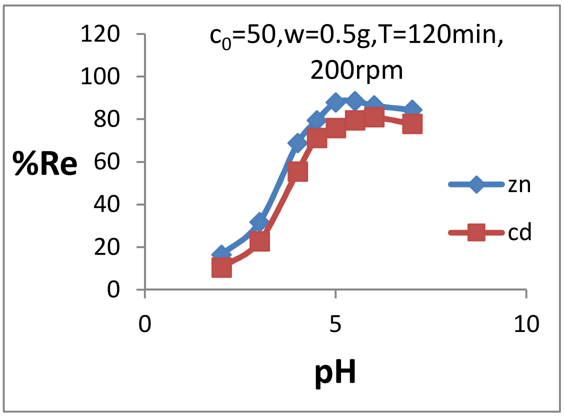
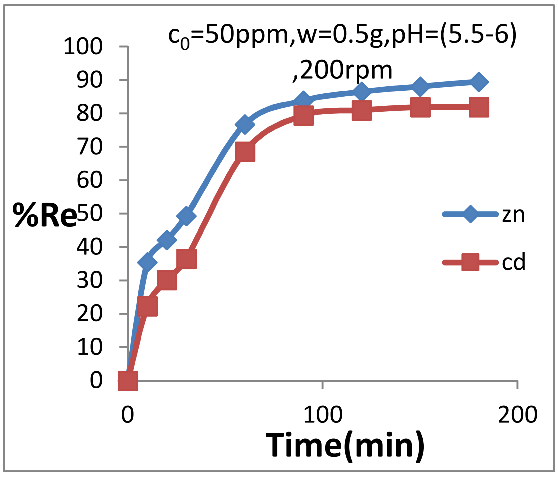


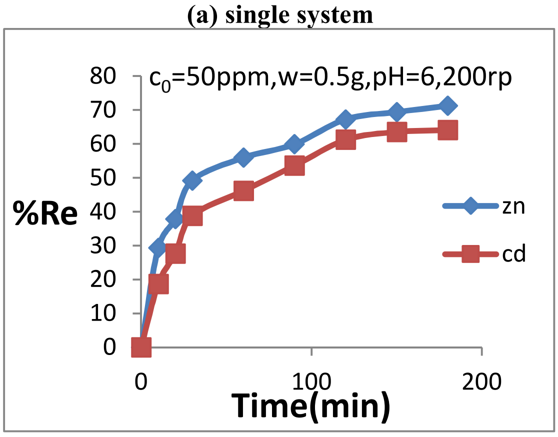
Figure 2: Percentages of cadmium and zinc ions removal efficiency onto cork stopper particles in the single system at different pH values

3.2 *Effect of contact time*

The percentage of Cd (II) and Zn (II) adsorbed was estimated at different contact time keeping the other parameters (solution pH= (5.5-6), dose of biosorbent= 0.5g, and speed of rotary shaker= 200 rpm) fixed. Fig. 3 represents the relation between the removal efficiency and different contact times in the single and binary systems. It was observed that the Cd (II) and Zn (II) biosorption increases as the contact time increases and it remains constant after reaching equilibrium. This is due to a larger surface area of the cork stopper particles at the beginning of the biosorption process. As the surface biosorption sites became exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the biosorbent particles. The maximum removal efficiencies of Cd (II) and Zn (II) for single system were (81.86,89.46)% respectively attained after about (150-180) min of shaking time ,while in binary system the removal of the tow metals decreased becous of the competition between ions onto the active sites presents on the surface of cork particles; the result agrees with that obtained by [8]and [1].



(a) single system



(b) binary system

Figure 3: Percentage of cadmium and zinc ions removal efficiency onto cork stopper particles in single and binary systems at different contact time

3.3 *Effect of agitation speed*

Fig.4 represents the relation between removal efficiency of cadmium and zinc ions onto cork stopper particles at different agitation speeds. It is observed that the removal efficiency of metal ions increased to an extend as the agitation speed increased. This is due to the fact that, a higher agitation speed decreases the film thickness and eventually eliminates film resistance. The decrease in removal efficiency after 200 rpm is due to stick a part of the biosorbent (cork stopper particles) on inside surface of the volumetric flask neck during the operation of the shaker which lowers biosorption of Cd (II) and Zn (II). Therefore, 200 rpm was taken as the optimum agitation speed where maximum removal efficiencies can be obtained. These results are analogous to that found by [13, 26]

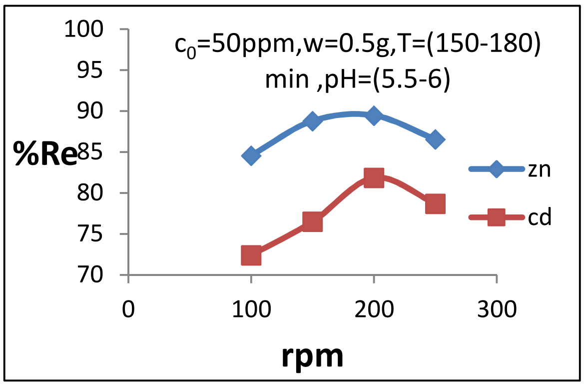
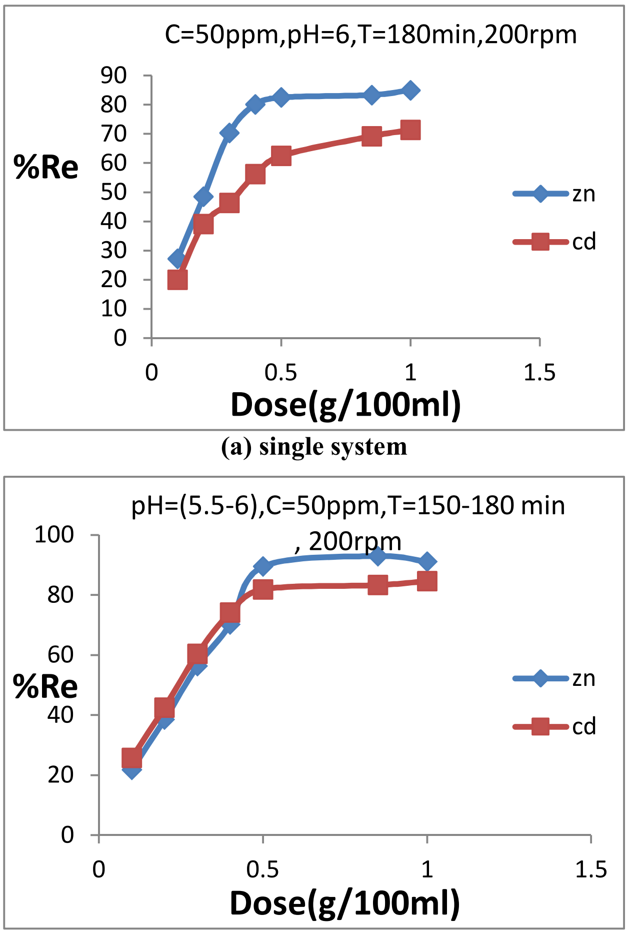


Figure 4: Removal efficiency of cadmium and zinc ions biosorbed onto cork stopper particles at different agitation speeds.

3.4 *Effect of biosorbent dose*

The effect of biosorbent dose (cork stopper particles) on the removal efficiency of Cd(II) and Zn(II) is shown in fig.5 which represents the relation between the removal efficiency of Cd(II) and Zn(II) at different doses of cork stopper particles in both single and binary systems. It is shown that, the removal efficiencies of the intended ions increases as the mass of the biosorbent increases. However, the removal efficiency increased from 25.74% to 82.62 % for cadmium ions and from 21.96% to90.11% for zinc ions as a single system, this is due to the increase in biosorbent surface area and the availability of more biosorption sites .in binary system it was found that, the removal of both metals ions reached its maximum value with biosorbent dose equal to 1gm.



(a) single system

(b) binary system

Figure 5: Removal efficiency of cadmium and zinc ions biosorbed onto cork stopper particles at different doses of biosorbent.

3.5 *Sorption Isotherms*

The sorption data parameters for Cd(II) and Zn(II) onto cork stopper particles for each model in single and binary systems were obtained by fitting the equations to the experimental data using Microsoft Excel as shown in Figures 6 ,7,and 8 for Langmuir, Freundlich, and Temkin models respectively. Tables 3 and 4 represent all parameters with correlation coefficient. From these tables the Langmuir model described the single sorption data slightly better than the other model depending on the value of coefficient of determination (R^2), and Extended Freundlich gives the best fitting for the experimental data of binary system.

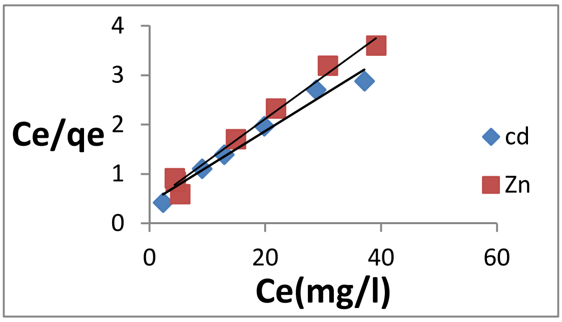


Figure 6: Langmuir isotherm model

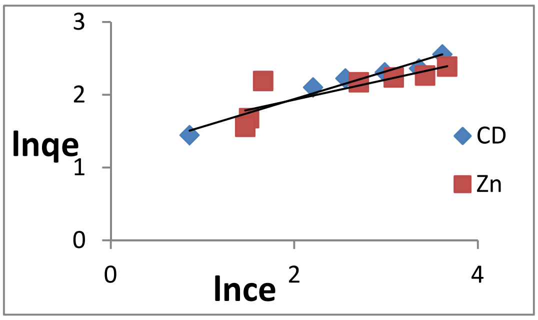


Figure 7: Freundlich isotherm model

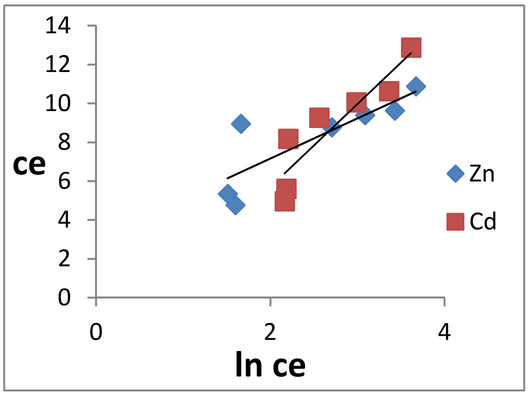


Figure 8: Temkin isotherm model

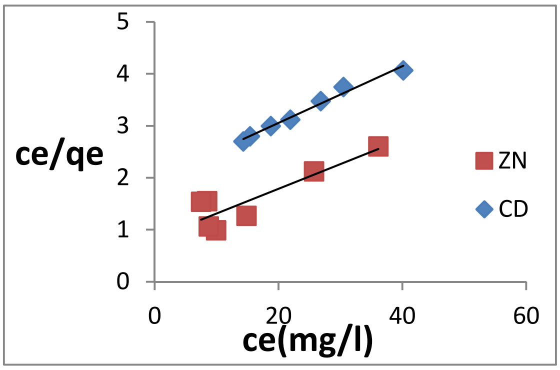


Figure 9: Extended Langmuir isotherm model

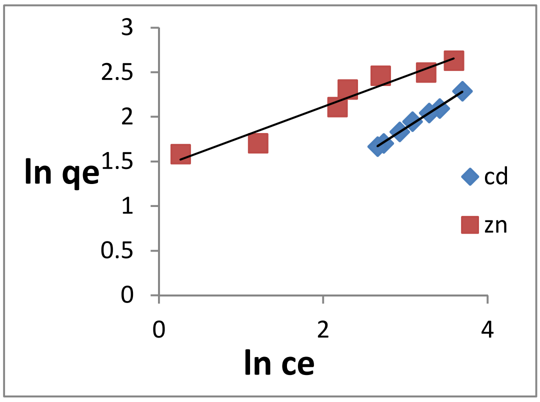


Figure 10: Extended Freundlich isotherm model

Table 3: Parameters of single solute isotherm for Cd^{+2} and Zn^{+2} onto cork stopper particles

Model	Parameters	Cd(II)	Zn(II)
Langmuir $q_e = \frac{q_{max} b C_e}{(1 + bC_e)}$	q_{max}(mg/g)	13.88	11.49
	b(l/mg)	0.412	0.346
	R^2	0.970	0.984
Freundlich $q_e = K_f C_e^{1/n}$	K_f (l/mg)	3.20	3.74
	n	2.63	3.62
	R^2	0.965	0.678
Temkin qe=(RT/b) ln(K_T Ce)	K_T (l/mg)	5.42	3.63
	B1=(RT/b) (KJ/mole)	4.257	2.0675
	R^2	0.837	0.694

Table 4: Parameters of binary solute isotherm for Cd^{+2}, and Zn^{+2} onto cork stopper particles

Model	Parameters	Cd(II)	Zn(II)
Extended Langmuir	q_{max}(mg/g)	18.315	21.08
	b(l/mg)	0.508	1.19
	R^2	0.981	0.788
Extended Freundlich	K_f (l/g)	0.238	3.88
	n	1.68	2.929
	R^2	0.995	0.949

3.6 *FT-IR analyses*

The FT-IR spectra before and after biosorption of cadmium and zinc ions (C_o=50mg/l, pH(5.5-6), rpm=200 ,and contact time (150-180) min) for (0.85-1) gm of cork stopper particles in a 100ml of Cd(II) and Zn(II) solutions were plotted to determine the vibration frequency changes of the functional groups in the biosorbents . The functional groups which were identified from the FT-IR spectra of the cork stopper particles are presented in figure 11 (before loaded (black), after loaded with Cd (II) (red), and after loaded with Zn (II) (blue)) and listed in Table 5.

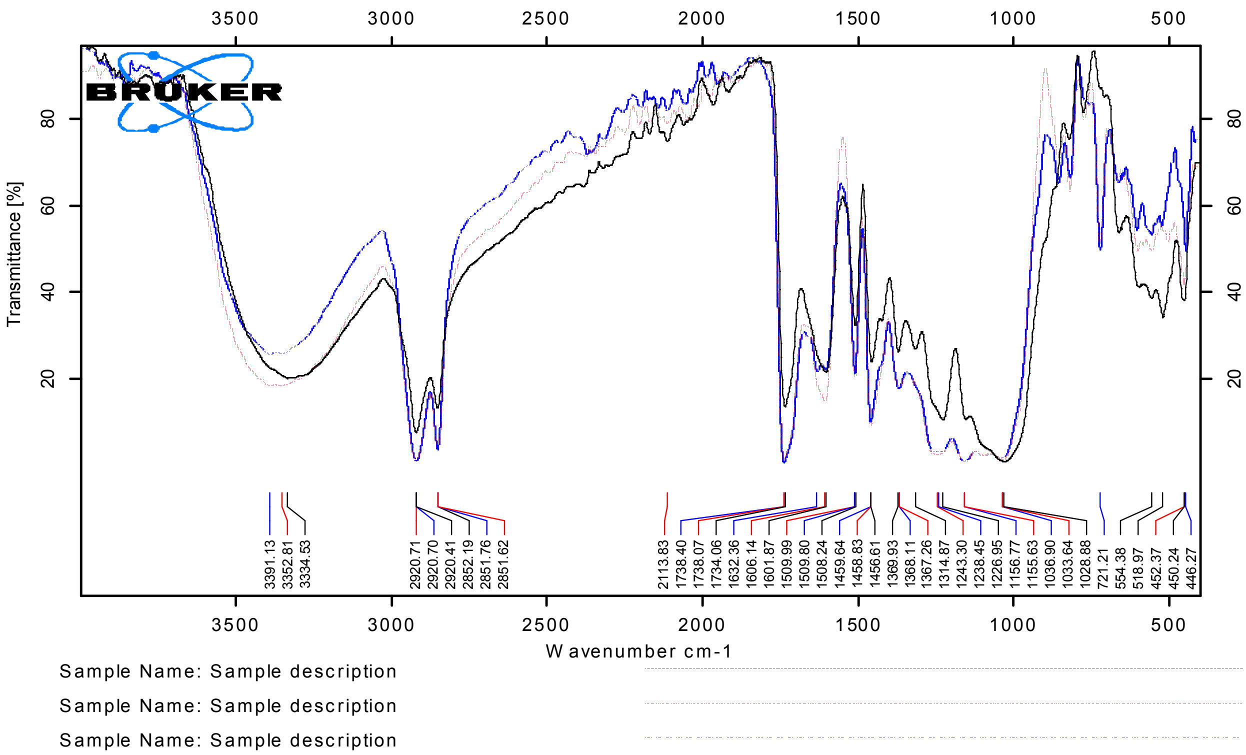


Figure 11: FT-IR spectra for cork stopper particles before and after loaded with 50 mg/l of Cd(II)and Zn(II).

Table 5: Functional groups responsible for cadmium and zinc ions biosorption onto cork stopper particles.

Assignment Functional Groups	Wave number (cm^{-1})		
	Before Adsorption cm^{-1}	After adsorption of Cd(II) cm^{-1}	After adsorption of Zn(II) cm^{-1}
Hydroxyl (OH)	3324.25	3351.89	3360.63
Alkane (C-H)	2852.45	2852.19	2921.53
Carbonyl (C=O)	1602.3	1629.59	1604.03
Carbonyl (C=O)	1508.71	1509.79	1509.30
Carboxylic acids and alcohol(C-O)	1029.75	1034.44	1153.94
Aromatic Compound	821.17	820.54	821.38
Aromatic Compound	775.76	775.33	721.24
Aromatic Compound	552.93	517.76	549.69
Aromatic Compound	455.88	447.96	455.72
Hydroxyl (OH)	3324.25	3351.89	3360.63
Alkane (C-H)	2852.45	2852.19	2921.53

The results indicated that carboxylic and aromatic functional group plays an important role in the biosorption process. Cadmium and zinc ions shows higher uptake for cork, probably due to the higher interaction of those metal ions towards the carboxylic and phenol groups in the cork.

3.7 *Kinetic Experiments and Models*

3.7.1 The optimum mass of cork stopper particles

The mass of cork stopper particles used for biosorption of cadmium and zinc ions was determined from the equilibrium related concentration of (C_e/C_o=0.05) using Langmuir equation with mass balance in one litter of solution as follows:

$$q_e = \frac{V_L(C_o - C_e)}{W_o} = \frac{q_m bCe}{1 + bC_e}$$

Thus;

$$W_o = \frac{V_L(C_o - C_e)(1 + bC_e)}{(q_m bC_e)} \tag{15}$$

The optimum mass of cork stopper particles was found to be (6.74, 8.91) gm for Cd (II) and Zn (II) respectively.

3.7.2 Optimum agitation speed

Fig.12 shows the concentration decay curves of solutes at different agitation speeds of (200, 400, 600 and 1000) rpm. It found that the optimum agitation speed needed to achieve C/C_o= 0.05 is 400 rpm for Cd (II) and 600 rpm for Zn (II). It is clear that, if the speed is above 400 rpm (in Cd (II) state) and 600 rpm (in Zn (II) state), the equilibrium relative concentration is less than 0.05.

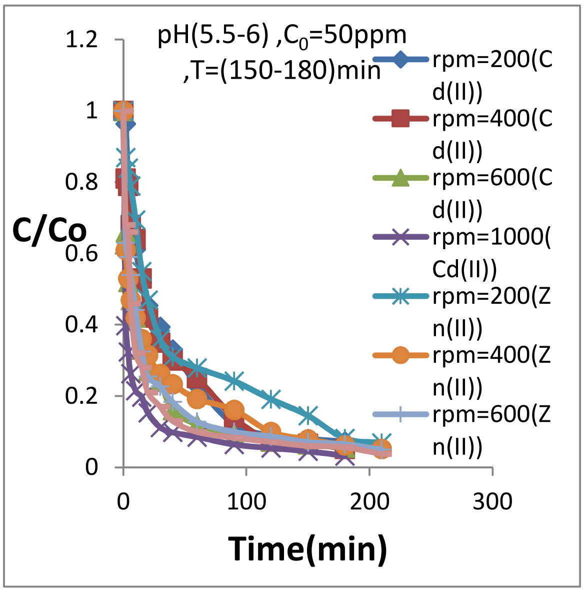


Figure 12: Concentration-time decay curves for biosorption of Cd (II) and Zn(II) at different agitation speeds

3.7.3 Determination of kinetic model coefficient

The kinetic constants of each model were obtained using Microsoft Excel Software. Comparisons of the kinetic models; pseudo-first order, pseudo-second order, and intra-particle diffusion results are depicted in figures 13, 14, and 15 and in Table 6.The results shows that pseudo first order model gives the best description for the experimental data (it have the highest value of R^2)

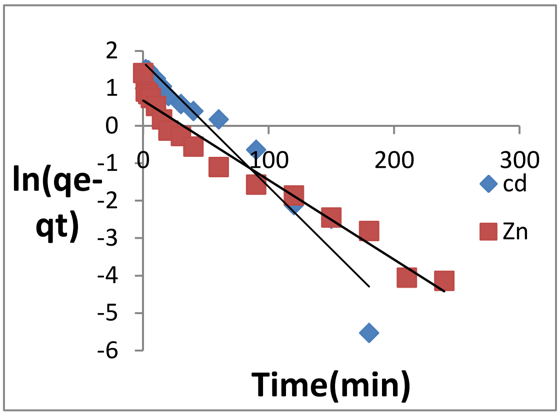


Figure 13: pseudo first order for biosorbtion of Cd(II) and Zn(II) onto cork particales.

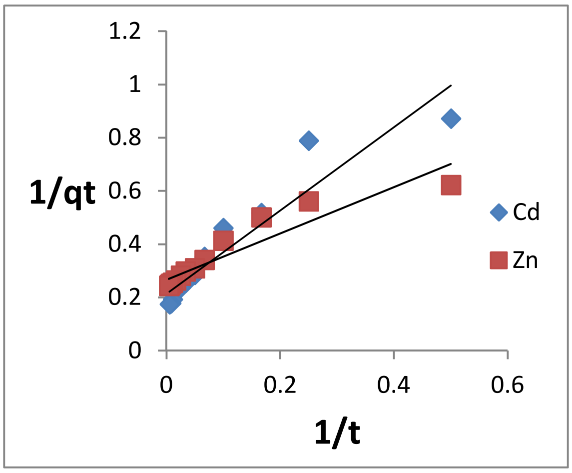


Figure 14: Pseudo second order for biosorption of Cd(II) and Zn(II) onto cork stopper particles

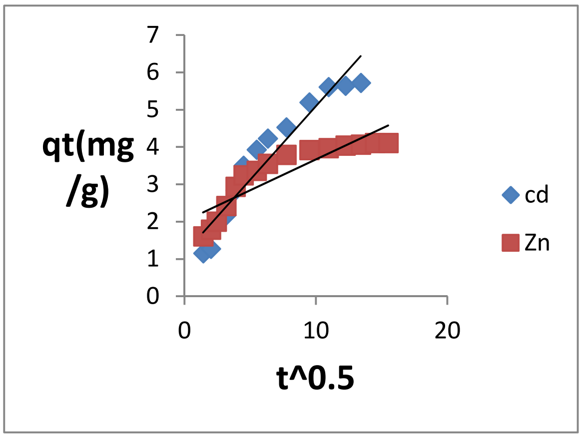


Figure 15: Intra-particle diffusion model for biosorption of Cd(II) and Zn(II) onto cork stopper particles.

Table 6: The kinetic constants for the biosorption of Cd (II) and Zn(II) onto cork stopper particles

Model	Parameters	Cd (II)	Zn(II)
Pseudo-first-order	q_e(mg/g)	5.81	4.126
	K_L (min^{-1})	0.033	0.022
	R^2	0.941	0.961
Pseudo-second-order	q_e (mg/g)	4.692	3.774
	K_s(g/mg.min)	1.565	0.872
	R^2	0.894	0.874
Intraparticle diffusion	C (mg/g)	1.151	2.010
	K_{id}(mg/g.$min^{0.5}$)	0.394	0.165
	R^2	0.916	0.790

4. Conclusion

The use of natural, economic, and abundant biosorbent (cork stopper particles) to remove Cd (II) and Zn (II) in single and binary systems from simulated wastewater by biosorption process was studied. In single system; the experimental results showed that the maximum removal efficiencies for Cd (II) and Zn (II) were (82.62, 90.96) % respectively with an initial concentration of 50 mg/l, pH value (5.5-6), and (0.85-1) g of biosorbent after (150-180) min contact time. pH 6 was taken as an optimum pH value for the removal of both metals in binary system. A set of equilibrium isotherm experiments were conducted and fitted with three models; Langmuir, Freundlich, and temkin. The biosorption were found to be of favorable type and Langmiur model gives the best fit to the experimental data with correlation coefficient equals to (0.97, 0.984) for Cd(II) and Zn(II) respectively in single system. While in binary system; extended freundlich isotherm model gives the best fit to represent the experimental data of this system with correlation coefficient equals to 0.995 for Cd (II) and 0.949 for Zn (II). The kinetic experimental data were used to analyze the effect of external film boundary layer .Three kinetics models were investigated and fitted with the experimental data, they are ; Pseudo-first order, Pseudo second order, and Intraparticle diffusion. It was found that the kinetics of both Cd (II) and Zn (II) biosorption onto cork stopper particles followed Pseudo first order model.

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الامتزازالتنافسي لايونات الكادميوم والزنك من المحاليل المائية للنظام الاحادي والثنائي باستخدام سدادات الفلين

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الخلاصة – يعرض هذا البحث إمكانية استخدام سدادات الفلين كمادة مازة لإزالة أيونات الكادميوم والزنك من المحاليل المائية.وأجريت تجارب الامتزاز للنظام الأحادي والثنائي بدراسة تأثير الدالة الحامضية,كمية المادة المازة, زمن التماس,سرعة الأهتزاز والتركيز الأبتدائي لايونات المعادن لايجاد أفضل الظروف للحد الأقصى من إزالة هذه الأيونات. وأظهرت النتائج بأن موديل Langmuir ذو تقارب أفضل قليلاً من موديل Freundlich وموديل تمكن. وقد أثبتت البيانات الحركيةلأمتزاز عنصري الكادميوم والزنك بأنها يمكن وصفها مع الدرجة الاولى اما العمليات المتعاقبة لأزالة ايونات الكادميوم والزنك بالنظام الأحادي والثنائي فقد أظهرت بأن كفائة أزالة الزنك اكبر من كفائة الازالة للكادميوم وأن كفائة الأزالة لكليهما قلت في النظام الثنائي.

الكلمات الرئيسية – أيونات المعادن الثقيلة، الامتزاز، البيانات الحركية، نماذج إيزوثيرم، دقائق سدادات الفلين، تنافس.