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Biosorption of Lead, Cadmium, and Zinc onto Sunflower Shell: Equilibrium, Kinetic, and Thermodynamic Studies

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Abstract

The present study deals with the application of an a bundant low cost biosorbent sunflower shell for metal ions removal. Lead, Cadmium and Zinc were chosen as model sorbates. The influences of initial pH, sorbent dosage, contact time, temperature and initial metal ions concentration on the removal efficiency were examined. The single ion equilibrium sorption data were fitted to the non-competitive Langmuir and Freundlich isotherm models. The Freundlich model represents the equilibrium data better than the Langmuir model. In single, binary and ternary component systems,Pb^{+2} ions was the most favorable component rather than Cd^{+2} and Zn^{+2} ions. The biosorption kinetics for the three metal ions followed the pseudo-second order kinetics indicating that the chemical sorption was the rate-limiting step. The thermodynamic parameters including free energy (ΔG^0), enthalpy and entropy changes for Pb^{2+},Cd^{2+} and Zn^{2+} ions indicated that the sorption process was feasible,spontaneous,and endothermic in the temperature range 20-50 ^{0} C .Desorption of the three metals ions from the biosorbent was effectively achieved in a 0.2 mol L^{-1} HCl solution.

Key Words: Biosorption, Heavy metals, Kinetics, Isotherm, Thermodynamics, Sunflower

Introduction

The use of heavy metals over the past few decades has been tremendously increased due to rapid industrialization in both developed and developing nations, which results an increased flux of metallic substances in the aquatic environment , [1]. Among various organic and inorganic pollutants, heavy metal ions are very toxic and carcinogenic in nature , [3]. Heavy metals enter into the food chain through the disposal of wastes into water bodies. According to the World Health Organization, the heavy metals of concern are lead, cadmium, chromium, zinc, copper, mercury, etc [4]. These metals are often derived from industries such as electroplating and battery factories, petrochemical refining, metal finishing, chemical manufacturing , [5]. Therefore, it is necessary to treat heavy metals effluents properly before they are discharged into the water bodies. In the present work, lead, cadmium, and zinc have been chosen as the contaminant in aqueous medium. Several technologies are available to remove heavy metals from wastewater before it can be launched into water bodies, such as: coagulation, flocculation, flotation, membrane separation, ionic, exchange resins and biological treatments, [6]. However, these methods are expensive, require sensitive operating conditions and produces huge quantity of sludge , [7]. Therefore , more economic,practical and efficient techniques are needed to meet the requirments of recovery and/or removal of metal ions. Biosorption of metal ions from aqueous solutions is a relatively new technology for wastewater treatment. Biosorption has been defined as the property of certain biomolecules to bind and concentrate selected ions or other molecules from aqueous solution. As opposed to a much more complex phenomenon of bioaccumulation based on active metabolic transport, biosorption by dead biomass is passive and based mainly on the affinity between the biosorbent and sorbate , [8] [9]. Biosorbents come under the following categories bacteria, fungi, algae, industrial wastes, agricultural wastes and other polysaccharide materials. Among them, agricultural wastes are the potential sources for producing biosorbents as they have no prominent utilization. Agricultural wastes are usually composed of lignin and cellulose as major constituents and may also include alcohols, aldehydes, ketones, carboxylic, phenolic and other groups, [10]. A number of studies have been focused on agricultural wastes that are capable of removing metals from wastewater such as apple wastes , [11], tea waste and coffee , [12], corn corps , [13], orange peel , [14], rice husk , [15], rice straw [16], wood apple shell , [1], coconut , [17], maize husk , [18] etc. Since industrial effluents may contain several matels , its necessary to study the simultaneous sorption of two or more metal ions and also to quantify the interactive effect of one metal ion on the other. Little information is available in literature for the simultaneous removal of cadmium, lead and zinc ions using sunflower shell. Therefore, the present work amis. to study the feasibility of using sunflower shell as an adsorbent for the removal of Cd^{+2}, Pb^{+2}, and Zn^{+2} ions from aqueous solutions. The main objectives of this work are: i) to study batch biosorption process in single, binary, and ternary systems, ii) to study the influence of initial pH solution, contact time, initial metal concentrations, and biosorbent dosage on the removal efficiency, iii) to investigate the isotherm model that can describe the biosorption process, iv) to study the thermodynamic and kinetics of metals biosorption to understand the mechanism of biosorption onto sunflower.

Materials and Methods

Biosorbent and sorbate preparation

To remove dirt and impurities, the sunflower shell was washed with tap water then distilled water, dried at 100 °C for 2 days in the oven to remove the moisture content. The dried sunflower shell was milled and sieved, and the average particle size of 0.5-0.6 mm of powdered sunflower shell was selected for biosorption experiments. The following are the major physical properties of sunflower shell: surface area (8.2 m^2/g), apparent density (0.98 g/cm^3), porosity (88.5 %), and moisture content (2.83 %).The stock solution (1000 mg/l) of each Pb^{+2}, Cd^{+2}, and Zn^{+2} ions were prepared by dissolving appropriate amount of each metal salt in distilled water and then stored in glass containers at room temperature. The three 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 flame atomic absorption spectrophotometer (AAS), type: SHIMADZU, Model: 7200,JAPAN, the initial pH of the working solutions was adjusted to the required value by adding 1 mol/l NaOH or HNO_3 using a pH meter (WTW, inoLab 720, Germany). To prevent heavy metal precipitation, some drops of HNO_3 was added to the collected samples. Prior testing in AAS, all the samples were refrigerated at approximately 40 ^{o}C.

Experimental Work

The effects of pH, biosorbent dose, agitation speed, and initial metal ion concentration on the removal efficiency of each metal were studied using classical approaches. In general, several stoppered conical flasks of 250 ml volume, each containing 0.5 g of biosorbent(except for dose effect) with 100 ml of 40 mg/l of each metal solution, were used. The suspension was shaken at 250 rpm for 2 h and temperature of 30 °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, and 7. Solutions with pH above 7 were excluded owing to the precipitation of metals as hydroxide may occur. The effect of biosorbent dose was studied in the range of 0.2 to 2 g. Different initial metal concentrations includ 10, 20, 40, 60 and 80 mg/l were used to study the effect of metal concentration . For the effect of contact time , the system was subjected to an agitation speed of 250 rpm, and the samples were collected from 1 to 360 min to be test for their metal remaining.

Isotherm Experiments

Biosorption of each metal onto sunflower shell was investigated in single, binary, and ternary systems. For single system, the experiments were carried out in 250 ml stoppered conical flasks containing 100 ml of pre-determined metal aqueous solution (10, 20, 30,40, 50, 60, 70, and 80 mg/l) and 0.5 g of sunflower shell, under constant shaking at 30±3 °C. The pH solution was adjusted to the best value based on the pH study. For each metal, eight flasks were placed in a shaker (Edmund Buhler, 7400 Tubingen Shaker-SM 25, Germany) at constant shaking speed (250 rpm) for 2 h. Upon equilibrium, the sorbent was separated from aqueous solution by using filter paper (WHATMAN, No.42, diameter 7 cm). The residual concentrations of metal were measured by AAS. The biosorption capacity at equilibrium conditions (q_e) was calculated by using the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \qquad \ldots(1)$$

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 (l), and m is the mass of the used adsorbent (g).

The percentage of removal (%) was calculated by using the following equation:

$$\%\ \text{Removal} = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \qquad \ldots(2)$$

For binary and ternary systems, the same procedure of single system experimentation was followed, in which the mixture of equal amount of metal solution (40 mg/l) was subjected to biosorption process by using 0.5g of sunflower shell.

Kinetic and Thermodynamic Experiments

For kinetic experiments 40 mg/l concentration of Pb^{+2}, Cd^{+2} and Zn^{+2} ion solutions were used. The sorption time varied between 0 and 180 min. In the isotherm experiments 0.5 g of biosorbent was added in 100 ml of $Pb^{+2,}$ Cd^{+2} and Zn^{+2} 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. The thermodynamic experiment was conducted using four flasks each flask containing 100 ml of 40 mg/l metal concentration, and the solution temperatures were 20, 30, 40, and 50°C (250 rpm for 2 h, at an optimum pH determined in the pH study). All determinations of each experiment were performed in triplicate and the average was used for this work.

Methods

Isotherm Model

In this study, the experimental isotherm data were fitted with the two well-known sorption isotherm models, namely, Langmuir and Freundlich models. These two models are presented in table (1). The Langmuir model is the simplest model for monolayer sorption onto a surface and assumes that all of the sorption sites have equal adsorbate affinity, [19]. The Freundlich isotherm model is used for homogenous systems in which the heat of sorption decreases in magnitude with an increasing extent of sorption , [20]. The Freundlich isotherm model describes the ratio of the amount of solute that is adsorbed onto a given mass of adsorbent to the concentration of solute in the solution.

Kinetic and Thermodynamic Model

The dynamics of the sorption process in terms of the order and the rate can be evaluated using the kinetic sorption data. A number of kinetic models have been used to describe the adsorption rate in batch operation. These models are pseudo-first order, pseudo-second order, and intraparticle diffution models as given in table (1). The pseudo-first-order kinetic model has been widely used to predict metal biosorption kinetics. The pseudo-first-order rate expression suggested originally by Lagergren is based on the solid capacity. The pseudo-second-order kinetic model is based on the assumption that the rate of sorption follows second-order chemisorptions , [21]. This model assumes that the metal molecule is sorbed onto two sorption sites on the sunflower peels surface. The possibility of intra-particle diffusion of sorbate onto the adsorbent by using the intra-particle diffusion model were studied. An intra-particle diffusion rate can be expressed in terms of the square root time. The mathematical dependence of q_t vs. $t^{0.5}$ is obtained if the sorption process is considered to be influenced by diffusion in the spherical particles and the convective diffusion in the solution. In addition, the thermodynamics parameters of the sorption process such as enthalpy changes (ΔH°), entropy changes (ΔS°), and Gibbs free energy changes (ΔG°) were used to determine the spontaneity of biosorption process. These parameters have been determined using Van't Hoff and Gibbs free energy equations, table (1).

Table (1), Equations for the sorption isotherm and kinetics models

Model	Equation	Linear expression	Reference
Langmuir	$q_e = \frac{q_m K_L C_e}{1+K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	**[22]**
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	**[23]**
Pseudo-first-order	$q_t = q_e\left(1 - e^{-k_1 t}\right)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	**[24]**
Pseudo-second-order	$q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	**[21]**
Intraparticle diffusion	$q_t = K_p t^{0.5} + C$	*same the original eq.*	**[25]**
Van't Hoff	$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$		**[26]**
Gibbs free energy	$\Delta G^\circ = -RT \ln K_c$		**[26]**

Where q_e is the sorption uptake (mg/g); C_e is the equilibrium concentration of the sorbate (mg/l); q_m is the maximum amount of the sorbate per unit weight of the sorbent (mg/g); K_L is the Langmuir constant and related to the free energy of sorption (l/mg); n is the Freundlich constant related to sorption intensity (g/l); K_F is the Freundlich constant related to the relative sorption capacity (mg/g);q_t is the metal uptake capacity (mg/g) at any time t; k_1 is the observed rate constant of pseudo-first-order kinetic model (1/min); and $k_2$is the observed rate constant of pseudo-second-order kinetic model (g/mg.min), K_p(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 ,K_c is the equilibrium constant (q_e/C_e), R is the universal gas constant (8.314 J/mol. K), ΔH° is the enthalpy of the sorption (kJ/mol), ΔS° is the entropy of the sorption (J/K.mol), ΔG° is the Gibbs free energy of biosorption (kJ/mol), and T is the solution temperature (K).

Results and Discussion

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 , [27]. The removal efficiency of Pb^{+2}, Cd^{+2}, and Zn^{+2} with pH ranging from 3 to 7 are studied and the results are depicted in Fig.(1a). From this figure, it can be seen that the best pH value for three metal removals was around 5. At lower pH, the active surface sites of the sunflower were either positively charged , [14], resulting the protons to compete with the metal ions, or dissociated**,** [28], which resultes in a decrease in the metal removal efficiency. At a pH range from 5 to 7, the removal percentage decreased because some active groups on the sunflower shell surface may be less protonated according to the fact of zeta potential**,** [29]. A similar trend was reported for the biosorption of Cd(II), and Cr(III) removal using garden grass**,** [30].

Effect of Biosorbent Dosage

The sorbent amount is also an important parameter to obtain the quantitive uptake of metal ions. Fig. (1b) shows the results of experiments that measured the effect of sunflower dosages on the removal percentage of metals. It can be seen for three metals, that the removal percent increased with increasing the amount of sorbent from (0.2-0.9 g) and then relatively remain constant. The removal efficiencies increases steadily with an increase in the sorbent concentration beyond 5 g/l. However the increase in sorbent dosage generally increases the amount of solute sorbed, due to the increased surface area of the sorbent, which in turn increases the number of binding sites**,** [31]. In actual applications, the optimal sorbent dosage should be defined as the lowest concentration that gives reasonable metal removal efficiencies and in present work the optimal dosage was about 0.5 g /100 ml for the three metals.

Effect of Contact Time

Fig. (1c) shows the effect of contact time on the removal efficiency of each metal. From this figure it can be seen that the Pb^{+2}, Cd^{+2}, and Zn^{+2} biosorption efficiency increased quickly within the first 60 min. The equilibrium condition was approximately attained within the first two hours 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 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 , [18].

Effect of Initial Metal Concentration

The initial concentration of Pb^{+2}, Cd^{+2}, and Zn^{+2} ions provides an important driving force to outweigh all mass transfer resistance of the metal between the aqueous and solid phases. Removal of these ions by 0.5 g sunflower shell dosage was investigated by employing the metal ions solutions with initial concentrations in the range of 10-80 mg/l at 120 min contact time and pH 5 , the results are depicted in Fig.(1d). From this figure, it can be seen that the percentage removal of Pb^{+2} decreased from 85.5 – 68.25%, for Cd^{+2} 79.5 – 61.3% and for Zn^{+2} from 72.3 – 60% with increasing the initial metal ions concentrations from 10-80 mg/l. According to**,** [32], 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**., [**33].

Kinetic Study

For any practical applications, the process design, operation control, and sorption kinetics are very important. Information on the kinetics of metals uptake is required for selecting optimum operating conditions for full-scale batch processes. In addition, the sorption kinetics in wastewater treatment is significant, as it provides valuable insights into the reaction pathways and the mechanism of sorption reaction [21].

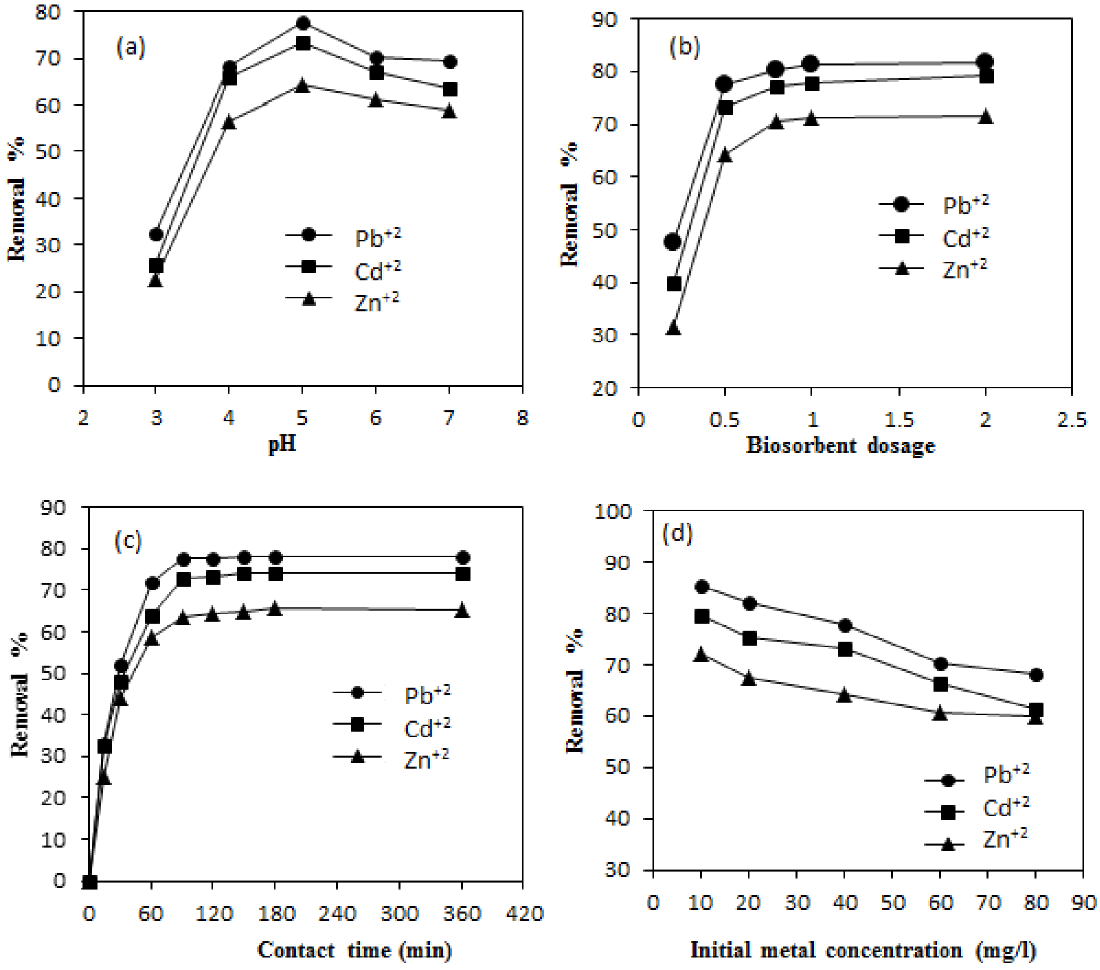

Fig. 1, Effect of: a) pH; b) biosorbent dose; c) contact time, and d) initial metal concentration on the removal efficiency

Fig. (2a) shows the evolution of uptake during Pb^{+2}, Cd^{+2}, and Zn^{+2} biosorption onto sunflower shell.

In order to evaluate the kinetic mechanism that controls the biosorption process, pseudo first-order and pseudo second-order models were tested to interpret the experimental data that are presented in Fig. (2a). The K_1 and q_e values for the pseudo-first-order kinetic model were obtained from the slope and intercept of the linear plots of $\ln(q_e-q_t)$ verses t (Fig. 2b), respectively, and the results are listed in table (2). Although a straight line with high correlation coefficients was obtained for the first order kinetic model,there is a deviation between experimentally observed biosorption capacity and that derived from this model. This suggest that for each metal the biosorption did not likely to explain by pseudo-first-order kinetic model. The second-order-kinetic model is based on the assumption that the sorption follows second-order chemisorption, [21]. The parameters of pseudo-second-order kinetics (k_2 and q_e) were calculated from the linear plots of t/q_t verses t (table (2)). The linear expression of this model is presented in Fig. (2c). A straight line with high correlation coefficients was obtained for the second-order-kinetic model much higher than the correlation coefficients derived from pseudo-first-order model fitting, also the deviation between the experimental and calculated biosorption capacity is less than that for pseudo-first order kinetic model. These results suggeste that the sorption process followes successfully pseudo-second-order kinetic model and the biosorption of Pb^{+2}, Cd^{+2}, and Zn^{+2} onto sunflower shell surface is most likely to involve chemical interactions leading to binding of the ions to the surface by bonding as strong as covalent binding , [34]. Similar phenomenon has been observed in the biosorpption of Pb^{+2}, Cd^{+2}, and Ni^{+2} on the modified orange peel , [7].

According to the intraparticle diffusion model, the plot of q_t vs. $t^{0.5}$ should be a straight line if this model is involved in the sorption process and if the plot passes through the origin then intraparticle diffusion is the sole rate-limiting step , [35]. Fig (4d) shows the intraparticle diffusion plot for Pb^{+2}, Cd^{+2}, and Zn^{+2} biosorption onto sunflower shell. It can be seen that this plot is multilinear, this suggests that the biosorption process is occurred in three phases **,.,** [36], [37]. The initial steeper section represents surface or film diffusion, the second linear section represents a gradual biosorption stage where intraparticle or pore diffusion is rate-limiting and the third section is the final equilibrium stage. When the straight line plot of intraparticle diffusion does not pass through the origin as shown in Fig (2.d), it indicates that this process is not the only rate-limiting step and other kinetic processes may also control the rate of sorption , [38]. Thus, there were three processes controlling the sorption rate but only one was rate- limiting in any particular time range. The parameters of the intraparticle diffusion model K_p and C were calculated from the slope and intercept of the second linear section in Fig (2d), respectively, and the results are presented in table (2). For the three metals, the law value of K_p (<1 $mg/g.min^{0.5}$) in the second section indicates a slower transfer rate. The high positive value of the intercept C provides information related to the thickness of the boundary layer , [39]. Larger intercept values indicate high boundary layer effect on the rate of sorption.

Biosorption Process

1. Single System

Sorption isotherm describes how sorbate molecule or ions are distributed between the solid phase and the liquid phase. Equilibrium isotherms are measured to determine the capacity of the sorbent for metal ions. This was obtained by the measurement of the equilibrium uptake for each metal at an initial concentration range from 10 to 80 mg/l. Fig. (3a) shows the typical equilibrium sorption of Pb^{+2}, Cd^{+2}, and Zn^{2+} ions on sunflower shell at 30 °C (single system). The biosorption capacity increased with the increase in the initial concentration of metals from 10 to 50 mg/l, and subsequently reached a plateau. A static biosorption capacity of 41.5, 37.1, and 33.8 mg/g of the sunflower sorbent was obtained for Pb^{2+}, Cd^{2+} and Zn^{2+} ions, respectively. Pb^{+2} demonstrated higher biosorption capacity, when compared with other metals, which can be attributed to high electronegativity of this metal. These results are in agreement with those reported by [40], who noted that more electronegative metal ions will be more strongly attracted to the surface of the adsorbent.

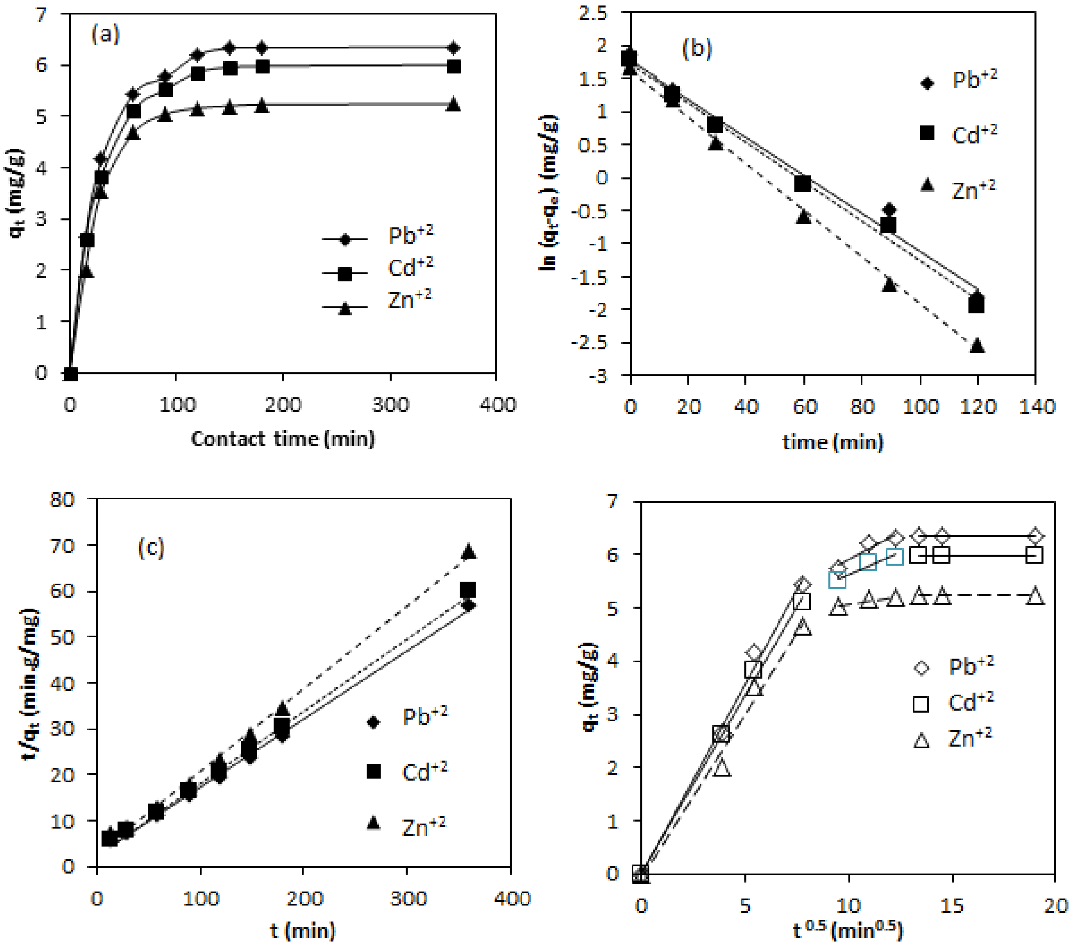

Fig. 2. Results of kinetic study of three metals biosorption onto sunflower shell a) uptake; b) pseudo first order; c) pseudo second, and d) intrapartical diffution model

Table (2), Kinetic parameters of Pb^{+2}, Cd^{+2}, and Zn^{+2} biosorption onto sunflower shell

Metal	q_{eq} (exp) (mg/g)	Pseudo-first-order model			Pseudo-second-order model			Intraparticle diffusion model		
		k_1 (1/min)	q_{eq} (cal.) (mg/g)	R^2	k_2 (g/mg.min)	q_{eq} (cal.) (mg/g)	R^2	K_p mg/g.min$^{0.5}$	C	R^2
Pb^{+2}	6.34	0.028	5.81	0.982	0.009	6.729	0.997	0.208	3.05	0.999
Cd^{+2}	6.00	0.0318	5.58	0.992	0.009	6.349	0.998	0.161	2.9	0.998
Zn^{+2}	5.16	0.033	4.697	0.996	0.010	5.540	0.997	0.058	2.64	0.998

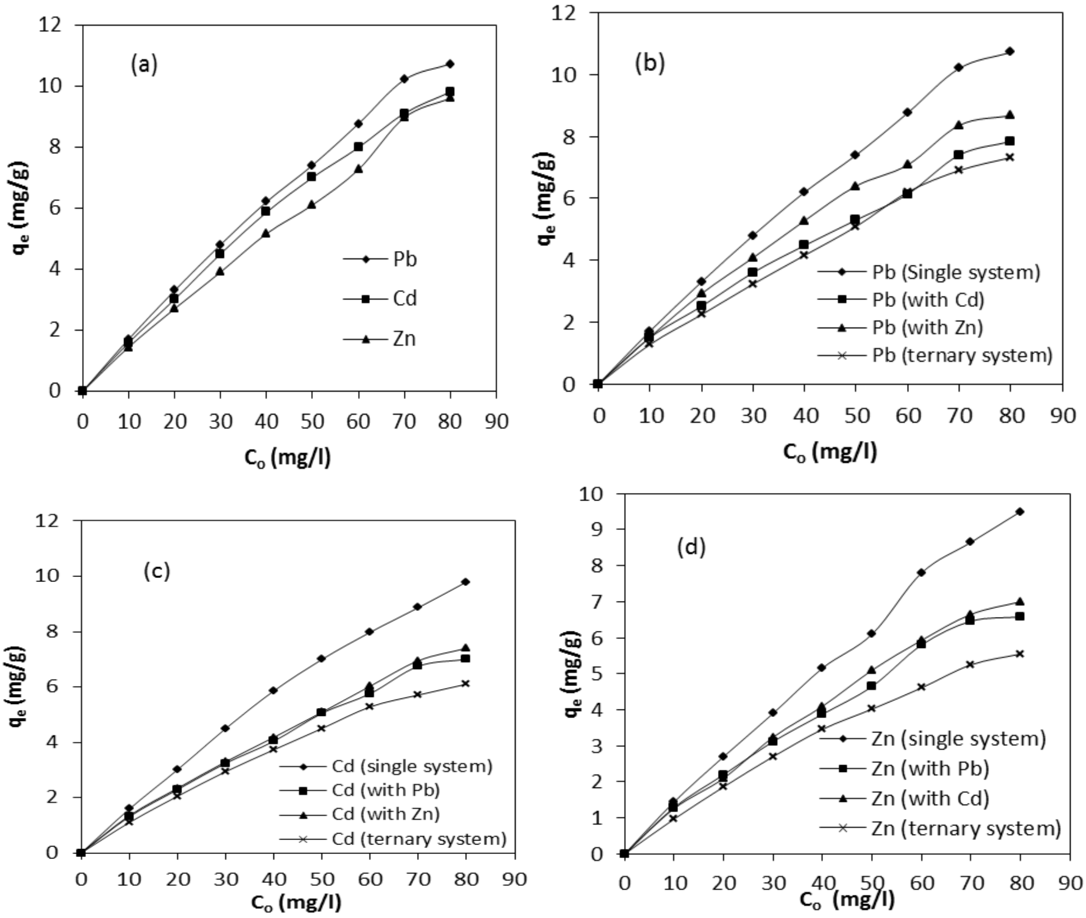

Fig.3, Biosorption isotherm: a) single system, b) Pb^{+2}, c) Cd^{+2}, and d) Zn^{+2} in binary and ternary systems

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 equilibrium data were correlated to Langmuir and Freundlich isotherm models. The linearized form of these two models is presented in Table (1). A plot of (C_e/q_e) vs. C_e yielded a straight line. The slope and the intercept of this line then yielded the values of the Langmuir constants q_m and K_L, respectively. The Freundlich coefficients could be determined from the plot of $\ln q_e$ verses $\ln C_e$. Table (3) shows the Langmuir and Freundlich model constants with the R^2 values. This table indicates that the Freundlich model provides the best fit as judged by its correlation coefficient for the three metals. Hence, the metals bind onto the heterogeneous surface of sunflower shell.

2. Binary and ternary systems

Sorption behaviors of metal ions in binary and ternary systems have been studied using the initial concentrations (10, 20, 30,40, 50,60,70, 80 mg/L) for each metal ion and the results are presented in Fig. (3 b-d). The sorption capacity for Pb^{+2} is greater than Cd^{+2} and Zn^{+2} in single, binary and ternary systems. As well as the biosorption of Zn^{+2} was the lowest one when compared with the biosorption of other metals in all systems. This behavior may be attributed to several reasons from which the hydrated ionic radius as well as the electronegativity of Pb^{+2} is higher than Cd^{+2}, and Zn^{+2} ions , [41]. The ions with hydrated radius smaller than the pore size are able to move easily within the pores. The hydrated ionic radius is as follows pb^{2+} (401 pm), Cd^{+2} (426 pm), Zn^{+2} (430pm). The decrease of sorption capacity in binary and ternary systems compared to the single metal systems observed for all metals reflects the existence of a competition between the metals for the binding sites present in the sorbent. It seems that the total metal sorption capacity decreases when increasing the number of metals present.

Thermodynamic Study

Desorption is a very important concern to allow for reusing the adsorbent and reduce process costs. It is desired that the adsorbent should be close to its original form, and should not lost its sorption ability after desorption, [32]. Experiments were carried out to desorb the metal ions (Pb^{2+}, Cd^{2+} and Zn^{2+}) from the metal loaded sunflower shell as a function of HCl concentration (mol/l).Volume of 100 ml with 40 mg/l metal concentration was agitated with 0.5 g sorbent. After the filtration procedure the metal ions loaded sorbent was dried in air. Then, treated with 50 ml of various concentrations of HCl to desorb the metal ions for 1 hour, the results are plotted in Fig. (4b). As can be seen from this figure, the desorption efficiency increased with increasing HCl concentration up to 0.2 mol/l. However, the desorption efficiencies were relatively insensitive to further increase in HCl concentration. Also, it can be seen that the metal which has the maximum biosorption uptake has the minimum recovery percent.

Table (3), Parameters of single solute isotherm for Pb^{2+}, Cd^{2+}and Zn^{2+} ions onto sunflower shell

Model	Parameters	Pb^{2+}	Cd^{+2}	Zn^{+2}
Freundlich	K, (mg/g)	1.166	1.02	1.203
	n	1.577	1.298	1.463
	R^2	0.995	0.985	0.993
Langmuir	q$_m$ (mg/g)	16.01	15.92	15.11
	b (l/mg)	0.062	0.051	0.039
	R^2	0.929	0.9374	0.918

Table (4), The thermodynamic parameters for the biosorption of Pb (II), Cd (II), and Zn (II) ions on sunflower shell

Metal	ΔH (J/mol)	ΔS (J/mol.K)	R^2	ΔG (J/mol)			
				293 K	303 K	313 K	323 K
Lead	18730	71.698	0.993	-2238.68	-3113.65	-3814.94	-4353.06
Cadmium	13924.28	53.531	0.989	-1624.8	-2537.28	-2927.56	-3243.99
Zinc	13968.35	51.343	0.991	-1152.22	-1503.92	-2204.13	-2602.17

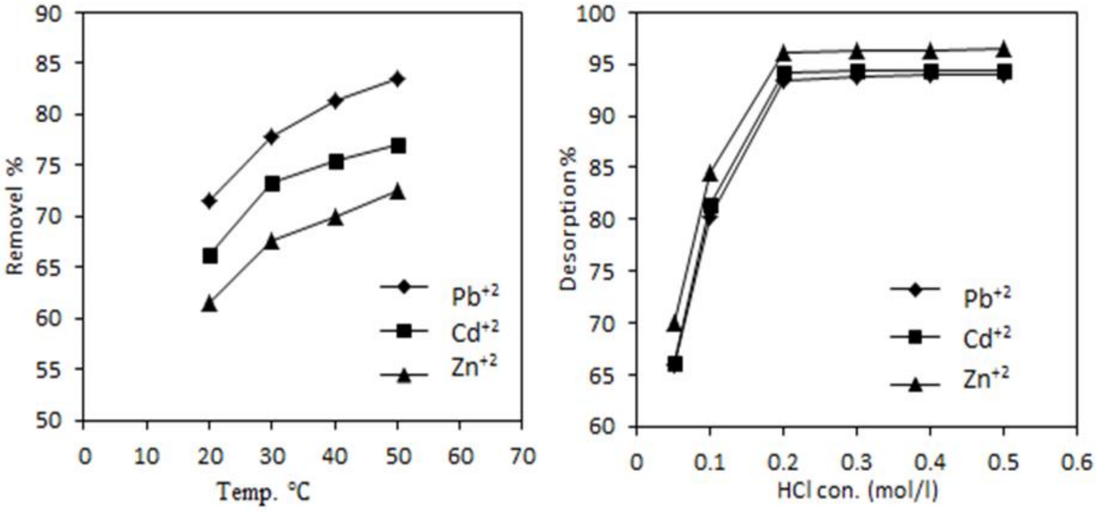

Fig. 4, a) Variation of percentage removal with temperature, b) Effect of HCl concentration on the desorption efficiencies

Conclusions

This study confirmed that sunflower shell is a promising biosorbent for lead, cadmium, and zinc removal from aqueous solutions. The biosorption equilibriums reached at 120 min contact time. The maximum biosorption capacity of 41.5, 37.1, and 33.8 mg/g on the sunflower sorbent was obtained at pH 5 for Pb^{2+}, Cd^{2+} and Zn^{2+} ions, respectively. The Freundlich isotherm model provides the best fit for the experimental isotherm data of the three metals. In the binary and ternary systems, Pb^{+2} demonstrated the highest biosorption capacity while Zn^{+2} was the lowest one owing to the competition condition. The pseudo-second-order kinetic model better explained the biosorption dynamics process for the three metals than the pseudo-first-order kinetic model. . Also the sorption process of Pb^{2+}, Cd^{2+} and Zn^{2+} ions are spontaneous and endothermic in nature. The biosorbed Pb^{2+}, Cd^{2+} and Zn^{2+} ions onto sunflower shell can be recovered using 0.2 mol/l HCl. Good efficiency to remove toxic metal ions was achieved by the usage of this agricultural by product.

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