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Biosorption of Pb (II) onto *Zygophyllum album* from Contaminated Wastewater: Equilibrium and Kinetics Studies

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Abstract: The biosorption of Pb (II) from aqueous solutions by *Zygopyillum album* (ZA) was investigated by using the batch technique. Effect of, pH, contact time, initial concentration of Pb (II) and initial adsorbent concentration on bioadsorption was investigated. The Langmuir, Freundlich, Temkin and Redlich-Peterson isotherms were applied to the obtained experimental data. The maximum adsorption capacity of Pb (II) onto ZA according to the Langmuir model was found to be 833 mg/g indicated that the *Zygophillum album* particles have great potential for the removal of Pb (II) from wastewater. The value of n is 5.18, indicates a favorable adsorption process. The experimental data were analyzed using different adsorption kinetic models viz., the pseudo-first and second-order models, Bangham's equation, intraparticle diffusion and Elovich models. Results show that the pseudo-second-order equation provides the best correlation for the biosorption process.

Key words: *Zygophyllum album* · Bioadsorption · Pb (II) removal · Aqueous solution · Equilibrium · Kinetic

INTRODUCTION

Heavy metals are found in the wastewater streams of industrial processes, including paint manufacture, leather tanning, battery manufacture, electroplating, plastics manufacturing, fertilizers, pigments, mining and metallurgical processes and others. Their removal has attracted much practical and academic interest owing to increased concern with their environmental impact. The most commonly used methods for the removal of metal ions from industrial effluents include chemical precipitation, solvent extraction, oxidation, reduction, dialysis/electrodialysis, flocculation, electrolytic extraction, reverse osmosis, ion exchange, evaporation and adsorption. The most common of these alternatives is chemical precipitation. However, the process has some limitations notably cost, low efficiency, labour-intensive operations and a lack of selectivity in the precipitation process [1]. Adsorption provides one of the most effective methods for removing heavy metal ions from aqueous solution [2]. The activated carbon is the most widely used adsorbent material. In fact, use of activated carbon is comparatively expensive with difficulties in regeneration and this has led to a large volume of work trying to develop low cost adsorbents [3]. Agricultural by-products are bioadsorbents mainly cellulosic in composition, constitute one of the most abundant renewable resources in the world. Agricultural wastes such as Haloxylon ammodendron [4], Alhagi residues [5, 6], sawdust [7] and sunflower stalks [8] are considered one of the low cost unconventional adsorbents, have been examined for potential use as inexpensive adsorbents for heavy metal removal.

Lead is a hazardous waste and is highly toxic to humans, plants and animals. It causes plant and animal death as well as anemia, brain damage, mental deficiency, anorexia, vomiting and malaise in humans [9, 10]. Lead is a substitute for calcium in bony tissues and accumulates there. The presence of lead in drinking water is known to cause various types of serious health problems leading to death in extreme cases [11]. The permissible limit of Pb is 0.01 mg/l1 in water. Biosorption is defined as a process in which solids of natural origin are employed for sequestration of heavy metals from an aqueous environment. Previous investigation [12] of *Zygophullum album* revealed that the plant contains ß-D-glucopyranoside, carbohydrates, tannins, lactones, proteins/amino acids, saponins, triterpene and flavonoid glycosides.

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The aim of the present work is to explore the possibility of utilizing ZA for the adsorption of Pb (II) from contaminated water. The effect of such factors as pH, adsorbent dose, adsorbate concentration, contact time and initial concentration was investigated. The kinetics of Pb (II) adsorption on the adsorbent was analyzed by fitting various kinetic models. Experimental equilibrium data were fitted to the Freundlich, Langmuir, Temkin and Redlich–Peterson isotherm equations to determine the best-fit isotherm equation. Error analysis was carried out to test the adequacy and the accuracy of the isotherm models.

MATERIALS AND METHODS

Materials

Adsorbent: Bio-adsorbent, *Zygophyllum album*, a desert plant is widely spread in Libya and Kingdom of Saudi Arabia. There is no previous report used *Zygophyllum album* as adsorbent material for removal of heavy metals. The roots were separated from the stems and leaves, washed with distilled water several times to remove the surface adhered particles and water soluble particles and dried at 80°C in an electric oven for 24 h and ground using a mixer and sieved to pass through a 100-200 mm. The roots were chosen because they contain the highest percentage of the cellulose content.

Reagents: Lead acetate, EDTA, ethanol, sodium carbonate and acetic acid were of analytical reagent grade supplied by Merck Company, Germany.

Methods

Bioadsorption Studies: The adsorbate solutions of 100-800 mg/l were prepared by dissolving certain weights of lead acetate in certain volumes of distilled water. The pH (2-4.5) of the solutions was adjusted with acetic acid or sodium carbonate solution. Equal volumes (100 ml of each) of the previously prepared metal ion solutions were placed in the corresponding number of 125 ml Erlenmeyer flasks each of which containing 0.05 g of the adsorbent and the whole flasks were shaken at 30°C in a thermostatic water-bath at 150 rpm for 2 h. At the end of agitation time, the metal ion solutions were separated by filtration. The blank experiments were simultaneously carried out without the adsorbent. The extent of metal ion adsorption onto adsorbent was calculated mathematically by measuring the metal ion concentration before and after the adsorption through direct titration against standard EDTA solution. The amount of lead adsorbed, q_e (mg/g) and percent removal of Pb (II) onto Zygophyllum album were calculated according to the following equations:

$$q_e = \frac{(C_o - C_e).V(l)}{W} \quad (1)$$

$$\text{Percent Removal} = \frac{C_i - C_f}{C_i} x100\% \quad (2)$$

where C_i and C_f are the initial and final concentrations of metal ion, mg/l.

Analyses

FT-IR Spectroscopy: The FT-IR spectra of *Zygophyllum album* particles were recorded on a Nexus 670 FT-IR spectrometer, Nicolet, USA, in the spectral range 4000-400 cm^{-1} with a resolution of 4 cm^{-1} using the KBr disk technique.

Error Analysis: In the single-component isotherm studies, the optimization procedure requires an error function to be defined to evaluate the fit of the isotherm to the experimental equilibrium data. The common error functions for determining the optimum isotherm parameters were, average relative error (ARE), sum of the squares of the errors (ERRSQ), hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD) and sum of absolute errors (EABS) [13]. In the present study, the average relative error (ARE) was used to determine the best fit in isotherm model as:

$$ARE = \sum_{i=1}^{n} \left| \frac{(q_e)_{\text{exp.}} - (q_e)_{calc.}}{(q_e)_{\text{exp.}}} \right|_i \quad (3)$$

RESULTS AND DISCUSSION

FT-IR Spectroscopy: The FT-IR spectral analysis is important to identify the characteristic functional groups which are responsible for adsorption of metal ions. The FT-IR spectrum of ZA (Fig. 1) shows distinct peaks at 3420.2, 2928.3, 1638.7, 1321.4, 1061.4 and 778 cm^{-1}. The bands at 3420.2 and 2928.3 are attributed to O-H stretching and C-H stretching, respectively. The peak observed at 1638.7 cm^{-1} is assigned to C-C bond stretch of aromatic rings. The peak at 1321.4 cm^{-1} refers to C-O bonding of phenols. In addition the bands at 1061.4 and 778 cm^{-1} indicate the vibration of C-O-C and O-H of polysaccharides and the bending modes of aromatic compounds in lignin, respectively.

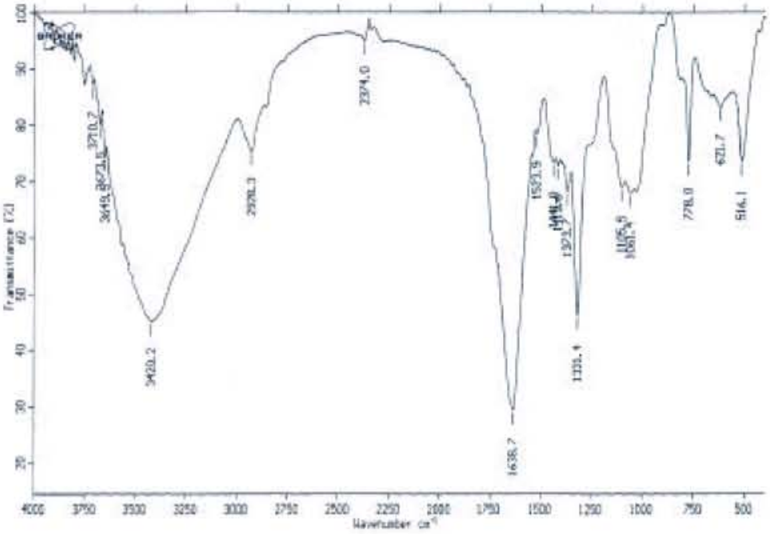

Fig. 1: FT-IR spectroscopy of *Zygophyllum album*.

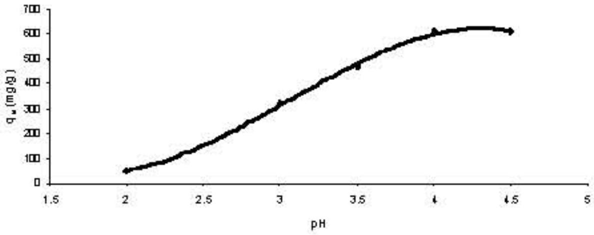

Fig. 2: Effect of pH on adsorption capacity of Pb (II) onto ZA at 30°C

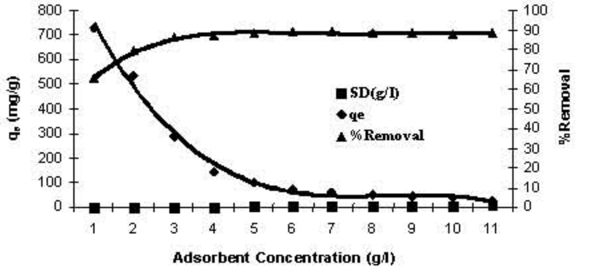

Fig. 3: Effect of adsorbent concentration on both capacity adsorption capacity and % removel of Pb (II) onto ZA at 30°C

Factors Affecting Adsorption of ZA

Effect of Initial pH: Adsorbate pH is an important parameter for the adsorption experiments. Fig. 2 shows the adsorption capacity of Pb (II) as a function of pH of the adsorbate at fixed adsorbent concentration, fixed agitation time, fixed adsorbate concentration at 30°C. It is clear from Fig. 2 that the adsorption capacity of Pb (II) onto ZA increases by increasing the pH from 2 to 4.5 within the range studied. Under highly acidic conditions (pH 2) the adsorption capacity of Pb (II) is the minimum because metal binding sites on the adsorbent were closely associated with H_3O^+ and restrict the approach of metal cations as a result of the repulsion forces. However, the adsorption increased with increasing the pH of solution since the adsorbent surface could be exposed with negative charge with subsequent attraction with positive charge occurring onto the adsorbate solution.

Effect of Adsorbent Concentration: The effect of adsorbent concentration on both adsorption capacity and percent removal of Pb (II) are shown in Fig. 3. It is clear from this figure that the percent removal of lead increases from 65 to 87 by increasing the concentration of adsorbent from 0.3 to 2 g/l and then remained at approximately the same level at higher adsorbent concentration. The increase in percent removal of Pb (II) with increasing adsorbent concentration in the first range could be attributed to the greater availability of the exchangeable sites of the adsorbent. The leveling of the percent removal at higher adsorbent concentration could be attributed to the blocking of the available active sites on the adsorbent surface. On the other hand, the adsorption capacity (q_e), or the amount of Pb (II) adsorbed per unit mass of adsorbent (mg/g), decreases by increasing the concentration of adsorbent (Fig. 3). The decrease in adsorption capacity with increasing the adsorbent concentration is mainly due to overlapping of the adsorption sites as a result of overcrowding of the adsorbent particles and is also due to the competition among Pb (II) ions for the surface sites [8].

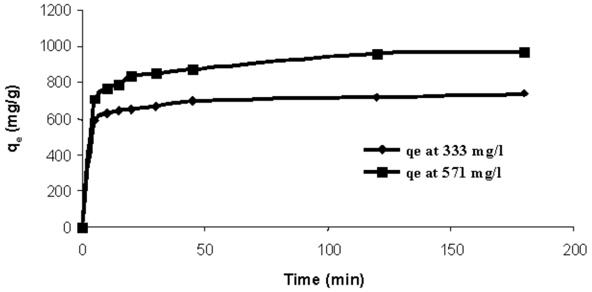

Fig. 4: Effect of contact time and initial adsorbate concentration on adsorption capacity of Pb (II) onto ZA at 30°C

Effect of Contact Time: Figure 4 shows the effect of agitation time on adsorption capacity of Pb (II) onto ZA by using the concentrations of 333 and 571 mg/l at fixed adsorbent concentration and at 30°C. The amount of Pb (II) adsorbed (mg/g) increases with the increase in agitation time and reached the equilibrium after 30 min. It is clear from Fig. 4 that the adsorption capacity depends on the concentration of the Pb (II) ions. The adsorption curves are singles and continuous indicating monolayer coverage of Pb (II) onto the adsorbent surface.

Adsorption Kinetic: In order to investigate the adsorption processes of ZA on the adsorbents, pseudo-first-order, pseudo-second- order, Bangham's equation, intra-particle diffusion and Elovich kinetic models were used.

Pseudo-First-Order Model: The pseudo-first-order equation [14] is:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4}$$

where q_t is the amount of adsorbate adsorbed at time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), k_1 is the pseudo-first-order rate constant (min^{-1}) and t is the contact time (min). The integration of Eq. (4) with the initial condition, $q_t = 0$ at $t = 0$, the following equation is obtained:

$$\log(q_e - q_t) = \log q_e - \frac{k_1.t}{2.303} \tag{5}$$

In order to obtain the rate constants, the straight line plots of log (q_e.q_t) against t for Pb (II) onto ZA have been tested. The intercept of this plot should give log q_e. However, if the intercept does not equal to the equilibrium uptake of metal ions, the reaction is not likely to be first order even if this plot has high correlation coefficient (R^2) with the experimental data [15]. For the data obtained in the present study, the plots of log (qe - qt) versus t as required by Eq. 5 for the adsorption of Pb (II) ions at initial concentrations of 333 and 571 mg/l by ZA (figure not show) gave correlation coefficients, R^2, which had low values for the two plots concerned. This indicates that the adsorption of Pb (II) onto ZA is not acceptable for this model.

Pseudo-Second-Order Model: The pseudo-second-order model is represented as [16]:

$$\frac{dq_t}{dt} = k_2(q_e - q_e)^2 \tag{6}$$

where k_2 is the pseudo-second-order rate constant (g /mg. min). Integrating Eq. (6) with the initial condition, $q_t = 0$ at $t = 0$, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{(k_2.q_e{}^2)} + \frac{t}{q_{t_t}} \tag{7}$$

where k_2 is the pseudo–second-order adsorption rate constant. This equation predicts that if the system follows pseudo-second-order kinetics, the plot of t/qe versus t should be linear. Plotting the experimental data obtained for the adsorption Pb (II) ions at initial concentrations of 333 and 571 mg/l onto ZA according to the relationship given in Eq. (7) gave linear plots with correlation coefficients, R^2, of 0.9997 for both concentrations of Pb (II) onto ZA, as shown in Figure 5 and listed in Table 1, thereby indicating the applicability of the pseudo-second-order kinetic equation to the experimental data. The experimental and calculated adsorption capacities for the two Pb (II) concentrations as well as the values of k_2 and R^2 are presented in Table 1. The first-order and pseudo-second-order models cannot identify the diffusion mechanism and the kinetic results were then subjected to analyze by the intra-particle diffusion model.

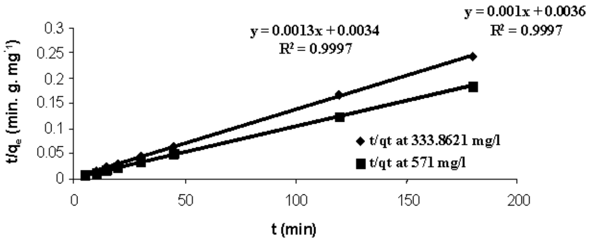

Fig. 5: Pseudo-second order reaction of Pb (II) onto ZA using different adsorbate concentrations at 30°C

Table 1: Kinetic parameters for adsorption of Pb (II) onto ZA at 30°C

	Pseudo-second order				Bangham's Equation			Intra-particle diffusion			Elovich Equation		
Init. Conc. (*mg/l*)	k_2	$q_{e(\exp)}$	$q_{e(calc)}$	R^2	k_0	α	R^2	k_P	C	R^2	α	β	R^2
295	0.0005	740	769	0.99	66	0.10	0.976	19.3	565.5	0.9816	131	0.02	0.977
494	0.0003	974	1000	0.99	365	0.12	0.982	30.6	684.4	0.9118	187	0.01	0.987

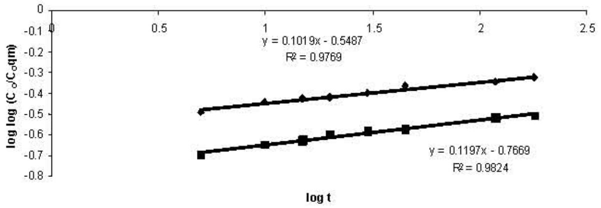

Fig. 6: Bangham's model of Pb (II) onto ZA using two different adsorbate concentration at 30°C

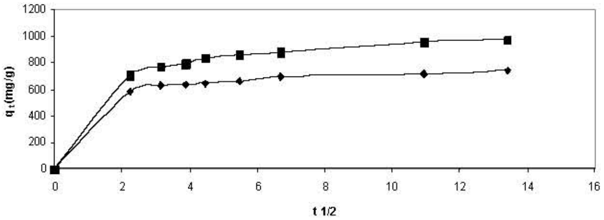

Fig. 7: Intra-particle diffusion model of Pb (II) onto ZA using two different concentraration at 30°C

Bangham's Equation: Bangham's equation [17] was employed for applicability of adsorption of Pb(II) onto ZA, whether the adsorption process is diffusion controlled.

$$\log\log(\frac{C_o}{C_o - q.m}) = \log(\frac{k_o m}{2.303V}) + \alpha \log t \qquad (8)$$

where C_0 is initial concentration of adsorbate (mg/l), V is volume of solution (ml), m is weight of adsorbent used, q is the amount of adsorbate retained at time t (mg/g), $\alpha(<1)$ and k_0 are constants. The double logarithmic plot, according to Eq. 8, yield satisfactory linear curves for the adsorption of Pb (II) by ZA. The correlation coefficient values, R^2 (Fig. 6) were 0.976 and 0.982 for the concentrations of 333 and 571 mg/l, respectively. This indicates that the adsorption of Pb (II) onto ZA is acceptable for this model and shows that the diffusion of adsorbate into the pores of the adsorbent was the rate-controlling step [17].

Intra-Particle Diffusion: The intra-particle diffusion model [18] can be expressed by the following equation:

$$q_t = k_P.t^{\frac{1}{2}} + C \qquad (9)$$

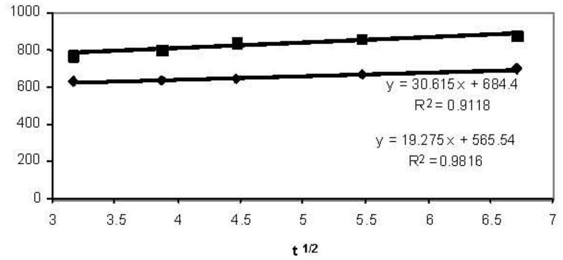

Fig. 8: Test of intra-particle diffusion model of Pb (II) onto ZA using two different concentrations at 30°C

where k_p is the intra-particle diffusion rate constant (mg g^{-1} $min^{-1/2}$) and q_t is the amount of solute adsorbed per unit mass of adsorbent. The data of solid phase metal concentration against time t at the initial concentrations of 333 and 571 mg/l of Pb (II) were further processed for testing the rate of diffusion in the adsorption process. Adsorption process incorporates the transport of adsorbate from the bulk solution to the interior surface of the pores in ZA. The rate parameter for intra-particle diffusion, kp for the two concentrations of Pb (II) are measured according to Eq. 9. The plots of q_t versus $t^{1/2}$ for the concentrations of 333 and 571 mg/l of Pb (II) are shown in Figure 7. The plots for two concentrations of metal ions have the same features, the initial portion (curved) followed by linear portion and plateau. The initial curved portion is attributed to the bulk diffusion and the linear portion to the intra-particle diffusion, while the plateau corresponding to equilibrium. The deviation of straight lines from the origin (Fig. 8) may be because of the difference between the rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of straight line from the origin indicates that the pore diffusion is not the rate-controlling step [19]. The values of k_p (mg $g^{-1}min^{-1}$) obtained from the slope of the straight lines (Fig. 8) are listed in Table 1. The values of R^2 for the two plots are listed also in Table 1. The values of intercept, C (Table 1) give an idea about the boundary layer thickness, i.e. the larger the intercept, is the greater the boundary layer effect [20]. These values indicate that the adsorption of Pb (II) onto ZA may be following the intra-particle diffusion mechanism.

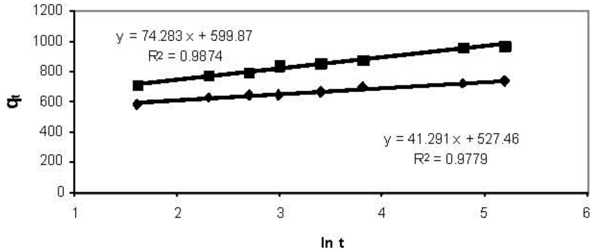

Fig. 9: Elovich model of Pb(II) onto ZA using two different adsorbate concentration at 30°C

Elovich Equation: The Elovich model equation is generally expressed as [21]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta . q_t) \tag{10}$$

where α is the initial adsorption rate (mg/g min) and β is the adsorption constant (g/mg) during any experiment. To simplify the Elovich equation, Chien and Clayton [21] assumed $\alpha\beta >> 1$ and by applying the boundary conditions q = 0 at t = 0 and $q_t = q_t$ at t = t, Eq. 11 become:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{11}$$

If Pb (II) adsorption onto ZA fits the Elovih model, a plot of q_e versus ln t should yield a linear relationship with a slope of $\frac{1}{\beta}$ and an intercept of $\frac{1}{\beta}\ln(\alpha\beta)$.

Figure 9 shows a plot of linearization form of Elovich model at the two concentrations studied. The slopes and intercepts of plots of q_t versus ln t were used to determine the constant β and the initial adsorption rate α. The correlation coefficients, R^2 for the two plots are listed in Table 1. The correlation coefficients for the Elovich kinetic model obtained at the Pb (II) concentrations of 333 and 571 mg/l were over 0.97. This indicates that the adsorption of Pb (II) onto ZA is acceptable for this model.

Effect of Adsorbate Concentration

Equilibrium Studies: Figure 10 shows the equilibrium adsorption isotherm of Pb (II) (q_e vs. C_e) onto ZA. The isotherm rises sharply in the initial stages for low C_e and q_e values. This indicates that there are plenty of radially accessible sites. Eventually a plateau is reached, indicating that the adsorbent is saturated at this level. In order to optimize the design of a sorption system to remove Pb (II) from contaminated water, it is important to establish the most appropriate correlation for the equilibrium curve. Four isotherm equations have been tested in the present study, namely; Langmuir, Freundlich, Temkin and Redlich-Peterson. The goodness-of-fit between experimental data and the model predicted values was expressed by the correlation coefficient (R^2, values close or equal 1). If the R^2 value is close to 1, it does not mean the fit is necessarily good. So, the conformity between experimental data and the model predicted values was expressed by the average relative error (ARE), is the discrepancy between the experimental data and the predicted values.

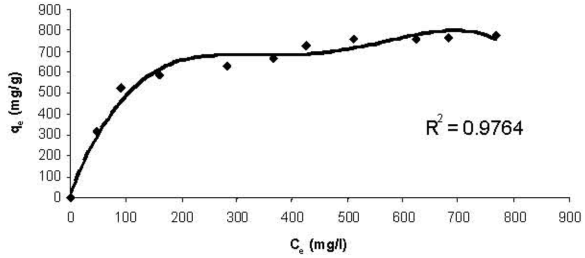

Fig. 10: Equilibrium adsorption isotherm of Pb (II) onto ZA at 30°C

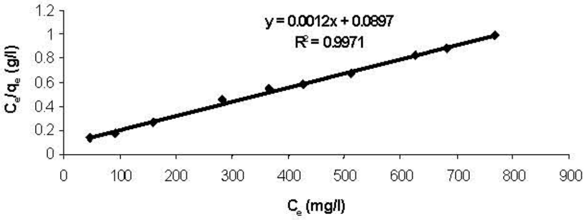

Fig. 11: Langmuri adsorption plot of Pb(II) onto ZA at 30°C

The Langmuir Isotherm: The widely used Langmuir isotherm has found successfully application in many real sorption processes [22] and is expressed as:

$$q_e = \frac{k_L . C_e}{1 + a_L . C_e} \tag{12}$$

wqhere C_e is the equilibrium concentration of Pb (II) ions (mg/l) and q_e is the amount of lead adsorbed (mg/g), while the constants K_L and a_L are the Langmuir constant (l/g) and Langmuir isotherm constant (l/mg), respectively. It is possible to represent Eq. (12) in a linearized form as:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + (\frac{a_L}{K_L}).C_e \tag{13}$$

The constants K_L and a_L give the theoretical monolayer solution capacity, Q_{max}. Therefore, a plot of C_e/q_e versus C_e gives a straight line (Fig. 11) of slope a_L/K_L and intercept of $1/K_L$. The values of the Langmuir constants a_L, K_L and Q_{max} with the correlation coefficient are listed in Table 2 for the Pb (II) onto ZA.

Table 2: Isotherm constants of parameter models for adsorption of Pb (II) onto ZA at 30°C

Isotherm Model	Parameters	Values
Langmuir	a_L	0.0134
	k_L	11.15
	Q_{max}	833
	R_L range	0.07-0.345
	R^2	0.9971
	ARE	1.7
Freundlich	k_F	10.39
	n	5.18
	R_2	0.9731
	ARE	3.5
Temkin	A_T	0.247
	b_T	16.57
	R^2	0.9739
	ARE	2.5
Redlich-Peterson	A	11.11
	B	76
	g	0.999
	R^2	0.9939
	ARE	1.5

The essential features of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which expressed by the following equation:

$$R_L = \frac{1}{(1 + b.C_0)} \tag{14}$$

where C_o is the initial concentration of Pb (II) and b Langmuir isotherm constant (l/mg). The values of R_L for the adsorption of Pb (II) ions at different initial concentrations onto ZA at 30°C are listed in Table 2. It has been reported that the effect of isotherm shape with a view to predicting if an adsorption system is favorable or unfavorable [23]. It is known that the value of $R_L < 1$ represents favorable adsorption and value of $R_L > 1$ represents unfavorable adsorption. In our case the value of R_L range was found to be 0.07- 0.345 ($0<R_L<1$). This vale indicates that the adsorption is favorable.

The Freundlich Isotherm: The well known Freundlich isotherm is often used for heterogeneous surface systems [24]. The Freundlich equation is given as:

$$q_e = K_F.C_e^{1/n} \tag{15}$$

A linear form of this expression is:

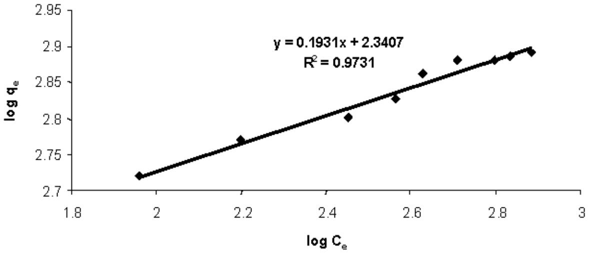

Fig. 12: Freundlich adsorption plot of Pb (II) onto ZA at 30°C

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{16}$$

where K_F is the Freundlich constant and n is the Freundlich exponent. K_F and n can be determined from the linear plot of log q_e versus log C_e (Fig. 12). The values of the Freundlich constants together with the correlation coefficient are presented in Table 2. The n value gives an indication to favorability of adsorption. The value of n was 5.18 (0<n<10) showing that the adsorption of Pb (II) ions onto ZA is favorable.

Tempkin Isotherm: The Temkin isotherm [25] has been used in the following form:

$$q_e = \frac{RT}{b_T}\ln(A_T C_e) \tag{17}$$

where R is the universal gas constant (8.31441 J^{-1} mol^{-1} K^{-1}), T is the absolute temperature (K), A_T is the Temkin isotherm constant (g/mg) and b_T is Temkin constant. The sorption data were analyzed according to the linear form of the Temkin isotherm as:

$$q_e = \frac{RT}{b_T}\ln A_T + (\frac{RT}{b_T})\ln C_e \tag{18}$$

Linear plots of q_e vs ln C_e at 30°C (Fig. 13) suggest the applicability of adsorption process of Pb (II) onto ZA on Temkin isotherm. The values of A_T and b_T were evaluated from the intercept and the slope of the plot and their numerical values along with R^2 are listed in Table 2. R^2 value (Table 2) of Pb (II) by ZA was over 0.97 indicating that the adsorption of Pb(II) ions on ZA is fitted well also on Temkin isotherm (obey the Temkin isotherm).

Redlich-Peterson Isotherm: Redlich-Peterson [26] is incorporated three parameters into an empirical isotherm. The Redlich-Peterson isotherm model combines elements from both the Langmuir and Freundlich equations and the mechanism of adsorption is a hybrid unique and does not follows ideal monolayer adsorption.

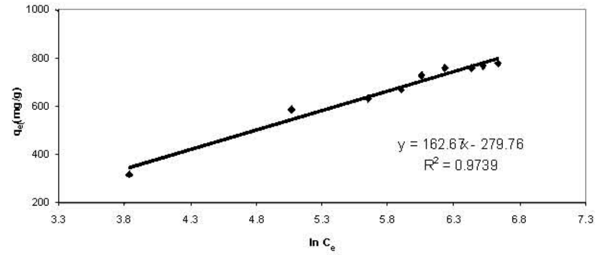

Fig. 13: Temkin adsorption plot of Pb (II) onto ZA at 30°C

The Redlich-Peterson equation is widely used as a compromise between Langmuir and Freundlich systems. The equation of this model is:

$$q_e = \frac{A.C_e}{1 + B.C_e^g} \tag{19}$$

where q_e is the amount of lead adsorbed (mg/g) at equilibrium, Ce (mg/l) is the concentration of adsorbate at equilibrium, A and B are the Redlich constants and g is exponent, which lies between 1 and 0. The application of this equation has been discussed widely and the limiting behavior is summarized as:

when g=1 the equation is reduced to the Langmuir model as:

$$q_e = \frac{A.C_e}{1 + B.C_e} \tag{20}$$

when g =0 the equation is reduced to Henery's law as:

$$q_e = \frac{A.C_e}{1 + B.} \tag{21}$$

The linear form of this model is obtained by applying logarithms to both sided of equation 23 as follows:

$$\ln(A\frac{C_e}{q_e} - 1) = g \ln C_e + \ln B \tag{22}$$

The three isotherm constants A, B and g can be evaluated from the linear plot presented by Eq. 22 and shown in Fig. 14 using a trial and error optimization method. A general trial and error procedure which is applicable to computer operation was developed to determine the correlation coefficient, R^2, for a series of values of A for the linear regression of ln [(A. C_e/q_e) -1] versus ln C_e at 30°C to obtain the best values of A which yields a maximum value of R^2. R^2 value (Table 2) of Pb (II) by ZA was over 0.99 indicating that the adsorption of Pb(II) ions on ZA is fitted well also on Redlich-Peterson isotherm (obey the Redlich-Peterson isotherm).

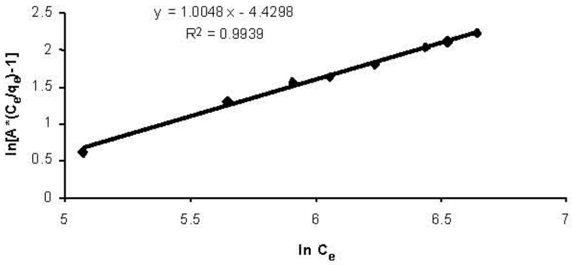

Fig. 14: Redlich-Peterson adsorption plot of Pb (II) onto ZA at 30°C

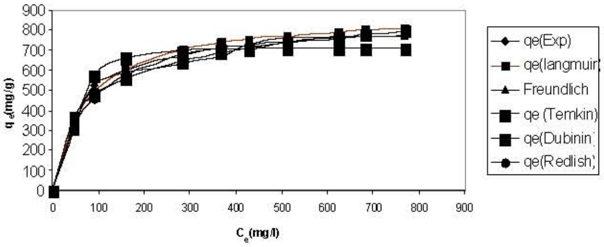

Fig. 15: Comparison between different isotherms of Pb(II) onto ZA at 30°CC

The comparison between the experimental data and the theoretical data obtained from isotherm models of Pb (II) onto ZA are shown in Fig. 15 which illustrates that the Temkin isotherm fitted the experimental data better than other isotherms.

Error Analysis: The use of R^2 is limited to solve linear forms of isotherm equation, which measures the difference between experimental and theoretical data in linearized plots only, but not the errors in non -linear form of isotherm curved. For this reason we use average relative error (ARE) to determine the best fit in isotherm models. For all isotherm models, the value of ARE for adsorption of Pb (II) onto ZA are calculated and presented in Table 2. The most obvious conclusions from these results are that the Temkin isotherm model has the lowest values for ARE and therefore fits the data better than the rest of isotherm models.

Mechanism of Bio Adsorption: The bio adsorbent contains various organic compounds (ß-D-glucopyranoside, carbohydrates, tannins, lactones, proteins/amino acids, saponins, triterpene and flavonoid glycosides) with polyphenolic groups that might be useful for binding metal ions. The ZA can be considered to be microporous biopolymer; therefore, pores are large enough to let Pb (II) ions through. The mechanism of Pb (II) adsorption on porous adsorbents may involve four steps: 1) diffusion of the ions to the external surface of adsorbent, 2) diffusion of ions into the pores of adsorbent and 3) adsorption of the ions on the internal surface of adsorbent, 4) chelation between the electrondonating nature of O- and N-containing groups in the ZA and electron-accepting nature in Pb (II).

CONCLUSIONS

This study shows that the desert plant, Zygophyllum album (ZA) is an effective adsorbent for the removal of Pb (II) from aqueous solution. The major advantage is the low cost recovery process that makes it suitable in water purification. The equilibrium data have been analyzed using Lanmguir, Freundlich, Temkin and Redlich-Peterson isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The suitability of the pseudo first- and second- order equations, Bangham's equation, intraparticle diffusion and Elovich kinetic models for the adsorption of Pb (II) onto ZA was discussed. The adsorption capacity of ZA for Pb (II) according to the Langmuir model was 833 mg/l at 30°C. The value of n is 5.18, indicates a favorable sorption process. On the basis of good sorption ability shown by ZA for Pb (II) by batch experiment suggests that this adsorbent has the potential of application for the removal of several heavy metals contained in wastewater. It may be concluded that may be used as low-cost, natural and abundant source for the removal of Pb (II) and it may be an alternative to more costly materials. It may also be effective in removing as well other harmful or undesirable species, present in the waste effluents.

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