

# Adsorption of Zn(II) ions from aqueous environment by surface modified *Strychnos potatorum* seeds, a low cost adsorbent

P. Senthil Kumar

SSN College of Engineering, Department of Chemical Engineering, Chennai, 603 110, India

\*Corresponding author: e-mail: senthilchem8582@gmail.com

The surface modified *Strychnos potatorum* seeds (SMSP), an agricultural waste has been developed into an effective adsorbent for the removal of Zn(II) ions from aqueous environment. The Freundlich model provided a better fit with the experimental data than the Langmuir model as revealed by a high coefficient of determination values and low error values. The kinetics data fitted well into the pseudo-second order model with the coefficient of determination values greater than 0.99. The influence of particle diffusion and film diffusion in the adsorption process was tested by fitting the experimental data with intraparticle diffusion, Boyd kinetic and Shrinking core models. Desorption experiments were conducted to explore the feasibility of regenerating the spent adsorbent and the adsorbed Zn(II) ions from spent SMSP was desorbed using 0.3 M HCl with the efficiency of 93.58%. The results of the present study indicates that the SMSP can be successfully employed for the removal of Zn(II) ions from aqueous environment.

**Keywords:** adsorption, isotherms, kinetics, shrinking core model, Zn(II).

## INTRODUCTION

Heavy metals such as lead, copper, cadmium, zinc, nickel, etc., are the most important pollutants throughout the world and many of them are toxic even at very low concentration. Among the heavy metals, zinc [Zn(II)] is one of the most important heavy metals and it is released into the environment from various natural and anthropogenic activities, such as acid mine drainage, galvanizing plants, ores and municipal wastewater treatments. Zinc ions are not biodegradable and can get accumulated easily in the living tissues. Further they can get readily absorbed into the human body, through the food chain. Higher concentrations of zinc ions can cause hazardous effects in plants and animals. Bureau of Indian Standards (BIS) has recommended the maximum permissible limit for zinc in drinking water as 5 mg/L<sup>1</sup>. A number of treatment technologies are available with a varying degree of success to remove heavy metals from wastewater. Some of them are chemical precipitation, ion exchange, electro-winning, electro-coagulation, cementation, solvent extraction, evaporation, reverse osmosis and electro-dialysis. However, most of them require substantial financial input initially, and their use is restricted because of the operational cost overriding the importance of water pollution control. However, these methods are either expensive or inefficient, when heavy metals exist in low concentrations<sup>2</sup>. And also they have several disadvantages that include incomplete metal ions removal, high reagent and energy requirements and generation of toxic sludge or other waste products that require proper disposal and further treatment. So, it is important to find new treatment technologies for the removal of heavy metals from wastewater. In the present day scenario, adsorption is proven to be one of the simplest and most effective treatment technologies for the treatment of wastewater containing heavy metal ions<sup>3-6</sup>. Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment throughout the world. In spite of the abundant uses of activated carbon, its applications are sometimes restricted due to their high cost. Therefore, researchers

are on the lookout for low-cost materials for water pollution control, particularly, where the cost factor plays a major role. For quite some time, efforts have been directed towards the development of alternative adsorbents which are efficient and cheap. They can be prepared from a wide variety of raw materials, which are abundant and possess high organic (carbon) content, low inorganic content and can be easily activated. Some of the low cost materials reported for the removal of zinc ions from the aqueous media are given as: cashew nut shell, maize husk (EDTA modified), sulphuric acid treated cashew nut shell, activated carbon from bagasse, xanthate modified magnetic chitosan, orange peel, rice bran, peat, coir, barely straw, *Azadirachta indica* bark, bagasse fly ash, physic seed hull, lignin, olive mill residue, banana peel, cork biomass, lignocellulosic substrate, etc.

The objective of the present study is to prepare an adsorbent by modifying the *Strychnos potatorum* seeds with the concentrated sulphuric acid, and apply it to remove the Zn(II) ions from aqueous solutions. The adsorption behaviours of the surface modified *Strychnos potatorum* seeds (SMSP) for Zn(II) ions are analyzed by fitting the experimental data in Langmuir and Freundlich adsorption isotherm models. To further investigate the adsorption behaviours, kinetic data obtained are also tested using the pseudo-first order, pseudo-second order, intraparticle diffusion, Boyd kinetic and shrinking core models. Desorption studies were also carried out to check the regeneration ability of the adsorbent.

## EXPERIMENTAL

### Materials and instrument

*Strychnos potatorum* seeds in the present studies for making adsorbent were collected from Pudukkottai District, Tamilnadu, India. The collected seeds were washed with double distilled water to remove the impurities and then it was dried under sun. The dried materials were ground into a fine powder using mixer grinder. The powdered seeds were then treated with concentrated sulphuric acid in a ratio of 2 : 1 (acid :

seeds) and this system was kept for about 24 h. The excess acid present in the system was removed by washing the material with the double distilled water until the pH of the solutions remained constant (pH = 7.0). Finally, the materials were dried in hot air oven at 80°C for 3 h, cooled, ground and sieved in the size of 0.354 mm and stored in airtight plastic box for further use. The prepared material was abbreviated as surface modified *Strychnos potatorum* seeds (SMSP) and this material was used as an adsorbent for the removal of Zn(II) ions from the aqueous solution. The FTIR and SEM analyses of the unmodified and modified *Strychnos potatorum* seeds were already discussed in our previous research work<sup>7</sup>. Aqueous solution of Zn(II) ions was prepared (500 mg/L) by dissolving the required quantity of ZnSO<sub>4</sub>·7H<sub>2</sub>O salt (Merck Chemicals, India) in double distilled water. The aqueous solution was diluted with double distilled water to obtain the Zn(II) ions synthetic wastewater of desired concentrations. The pH of the solution was adjusted to the required value with 0.1 N NaOH or 0.1 N HCl. The pH of solution was measured with a Hanna pH meter using a combined glass electrode (HI 98107, Hanna Equipments Private Limited, Mumbai, India). The concentration of Zn(II) ions in the solutions was measured by SL176 Atomic absorption spectrometer, AAS (Elico, India).

#### Batch adsorption experiments

Batch adsorption experiments were performed using 0.40 g of SMSP with 100 mL of Zn(II) ions solution of known concentrations (100–500 mg/L) in 100 mL stoppered conical flasks, at an optimum solution pH of 5.0 and at the temperature of 30°C. The mixtures of SMSP and the Zn(II) ions solution were shaken in an orbital incubation shaker (Royal Testing Equipment, Chennai, India) at 180 rpm. After the target contact time was reached, the suspensions were centrifuged (5000 rpm, R-24 REMI Centrifuge, India) to separate the spent adsorbent and supernatant. The supernatant was analyzed for Zn(II) ions using an AAS. All the batch adsorption experiments were carried out in duplicates. The percentage removal of Zn(II) ions was calculated by the following expression:

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where  $C_i$  and  $C_f$  are the initial and final Zn(II) ions concentrations in the solution (mg/L), respectively. The amount of adsorbed Zn(II) ions by the SMSP at equilibrium,  $q_e$  (mg/g), was calculated by using the following expression:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

where  $C_e$  is the concentration of Zn(II) ions in the solution at equilibrium (mg/L),  $V$  is the volume of Zn(II) ions solution (liter) and  $m$  is the mass of the SMSP (g). The amount of Zn(II) ions adsorbed onto the SMSP at time  $t$ ,  $q_t$  (mg/g), was estimated by the following expression:

$$q_t = \frac{(C_i - C_t)V}{m} \quad (3)$$

where  $C_t$  is the concentration of Zn(II) ions in the solution at time  $t$  (mg/L),  $V$  is the volume of Zn(II) ions solution (liter) and  $m$  is the mass of the SMSP (g).

#### Batch desorption experiments

Batch desorption of Zn(II) ions from the spent SMSP was conducted with varying concentrations of a HCl solution (0.1–0.35 M). 0.30 g of spent SMSP was transferred to stoppered conical flasks containing 100 mL of the HCl solution. The bottles were shaken at 30°C in a rotary shaker. The adsorbent was then removed by filtration. The concentrations of Zn(II) ions in the aqueous solutions were determined by using the AAS, to evaluate the extent of desorption.

## RESULTS AND DISCUSSION

#### Adsorption isotherms

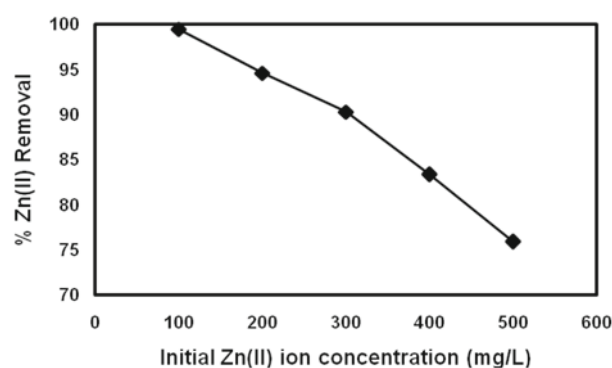
The effect of initial Zn(II) ions concentration on the removal of Zn(II) ions by SMSP is shown in Fig. 1. It can be seen that the removal percentage of Zn(II) ions was decreased with the increase in initial Zn(II) ion concentration. At lower Zn(II) ions concentration, Zn(II) ions in the solution would interact with the active sites of the SMSP and thus facilitated maximum adsorption. At higher Zn(II) ions concentration, many Zn(II) ions leave adsorbent due to the saturation of the active sites of the SMSP. This suggested that energetically less favourable active sites become involved with increase in concentration of Zn(II) ions in the solution.

The Langmuir<sup>8</sup> and Freundlich<sup>9</sup> adsorption isotherm models were employed to fit the data observed from the effect of initial Zn(II) ions concentration studies. The non-linear form of Langmuir adsorption isotherm model is given as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

and the separation parameter from the Langmuir equation is given as follows:

$$R_L = \frac{1}{1 + K_L C_o} \quad (5)$$



**Figure 1.** Effect of initial Zn(II) ions concentration on the adsorption of Zn(II) ions onto the SMSP (Zn(II) ions concentration = 100–500 mg/L, pH = 5.0, SMSP dose = 0.4 g, volume of sample = 100 mL, equilibrium time = 30 min and temperature 30°C)

The non-linear form of Freundlich adsorption isotherm model is given as follows:

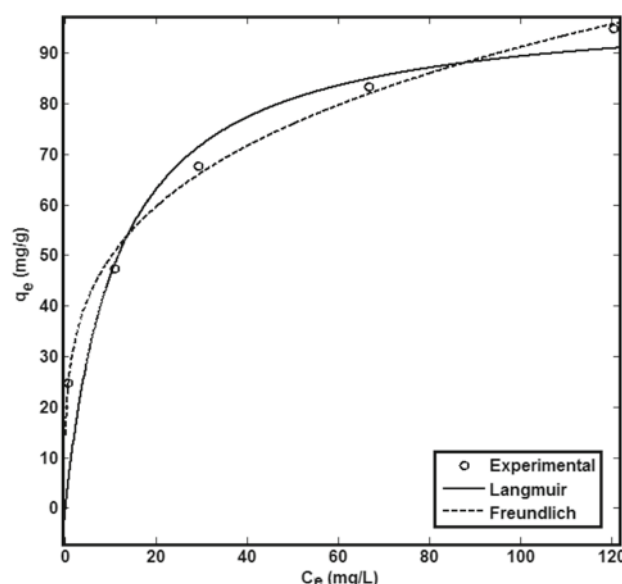
$$q_e = K_F C_e^{1/n} \quad (6)$$

where  $q_e$  (mg/g) and  $C_e$  (mg/L) are the amount of Zn(II) ions adsorbed onto the SMSP and the concentration of Zn(II) ions in solution at equilibrium, respectively;  $q_m$  is the maximum monolayer adsorption capacity of the SMSP for the Zn(II) ions (mg/g),  $K_L$  is the Langmuir constant related to the affinity of the Zn(II) ions to the SMSP (L/mg),  $C_0$  is the initial concentration of Zn(II) ions in the solution (mg/L),  $K_F$  is the Freundlich constant ((mg/g)(L/mg)<sup>(1/n)</sup>) related to the adsorption capacity and  $1/n$  is the Freundlich exponent related to the adsorption intensity (L/g)<sup>2-7</sup>.

The adsorption isotherm parameters, error values (SSE, Sum of Squared Error and RMSE, Root Mean Squared Error) and coefficient of determination ( $R^2$ ) values were calculated from the plot of  $C_e$  versus  $q_e$  (Fig. 1 (b)) and the values were given in the Table 1. As seen from the Table 1, the Freundlich adsorption isotherm model is able to provide a better fit to the experimental data than the Langmuir adsorption isotherm model. This indicates that the adsorption of Zn(II) ions onto the SMSP is a multilayer adsorption process. The parameter,  $1/n$ , in the Freundlich model is related to the intensity of adsorption, and the values of  $n$  in the range of 1–10 showed favourable adsorption process<sup>10</sup>. Table 1 indicates that the SMSP have higher affinity and adsorption capacity for Zn(II) ions. The parameters of Langmuir isotherm were found to be:  $q_m$  value of 98.75 mg/g and  $K_L$  value of 0.092 (L/mg). The values of separation parameter,  $R_L$ , were calculated by the above Eq. (5) and the values are in the range of 0.098–0.021 for an initial Zn(II) ions concentration of 100–500 mg/L, respectively. The calculated  $R_L$  values are in the range of 0–1, indicates the favourable adsorption process<sup>11</sup>. The maximum monolayer adsorption capacity ( $q_m$ ) of the SMSP was compared with the other adsorbents in order to evaluate the efficiency of the SMSP in the removal of Zn(II) ions. Table 2 contains the  $q_m$  values of the different adsorbents for the adsorption of Zn(II) ions from the aqueous solution. The  $q_m$  value of the SMSP for Zn(II) ions removal was higher than that of the majority of adsorbents listed in the Table 2. Therefore, it can be identified that the SMSP has adequate potential for the adsorption of Zn(II) ions from the aqueous solutions.

### Adsorption kinetics

Figure 2 (a) illustrates the effect of contact time on the removal of Zn(II) ions from aqueous solution using SMSP. This result revealed that the adsorption of Zn(II) ions is fast and the equilibrium was reached by 30 min of contact time. The results shows that the removal of



**Figure 2.** Adsorption isotherms for the removal of Zn(II) ions by SMSP (Zn(II) ions concentration = 100–500 mg/L, pH = 5.0, SMSP dose = 0.4 g, volume of sample = 100 mL, equilibrium time = 30 min and temperature 30°C)

Zn(II) ions increases with increasing contact time. From the results, it was observed that the removal of Zn(II) ions increased very rapidly at initial stage of contact time. However, after this contact time, the rate of adsorption decreased and became slower near the equilibrium condition. This may be due to the saturation of Zn(II) ions adsorption by the functional groups present in the SMSP surface, while the remaining Zn(II) ions were adsorbed by the pores of the SMSP inside the surface of the adsorbent. This phenomenon occurred due to the presence of large number of pores and vacant sites on the SMSP surface. Therefore, the higher removal of Zn(II) ions by the SMSP was observed at the initial stages of adsorption process. After certain time, the vacant sites get decreased and the Zn(II) ions were difficult to occupy due to the repulsive forces between the Zn(II) ions and the SMSP surfaces.

The different kinetic models have been applied to explain the removal of metal ions from the aqueous solution, whereas the most often used are Lagergren pseudo-first order<sup>12</sup> and pseudo-second order<sup>13</sup> kinetic equations. For the evaluation of the adsorption kinetics of Zn(II) ions, the adsorption kinetic data were applied to the pseudo-first order and pseudo-second order kinetic equations.

The pseudo-first order kinetic model assumes that the rate of change of the solute uptake to be proportional to the difference in the saturation concentration and the amount solid uptake with the time, i.e. the rate of occupation of adsorption sites is proportional to the number

**Table 1.** Langmuir and Freundlich isotherm constants for Zn(II) ions adsorption onto the SMSP

Isotherm Model	Parameter	$R^2$	SSE	RMSE	Equation
Langmuir	$q_m = 98.75$ (mg/g) $K_L = 0.092$ (L/mg)	0.8597	441.7	12.13	$q_e = \frac{9.085 C_e}{1 + 0.092 C_e}$
Freundlich	$K_F = 27.38$ ((mg/g)(L/mg) <sup>(1/n)</sup> ) $n = 3.828$ (g/L)	0.9946	16.91	2.374	$q_e = 27.38 C_e^{0.261}$



of unoccupied sites. The linear form of the pseudo-first order kinetic model is given by the following expression:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

where  $q_e$  is the equilibrium adsorption capacity (mg/g),  $q_t$  is the adsorption capacity at time  $t$  (mg/g),  $k_1$  is the pseudo-first order rate constant ( $\text{min}^{-1}$ ) and  $t$  is the time (min). The pseudo-first order kinetic parameters can be calculated from the slope and intercept of the plot  $\log(q_e - q_t)$  versus time (Fig. 2 (b)) and the values were listed in Table 2.

The pseudo-second order kinetic model assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. The non-linear form of the pseudo-second order kinetic model is given by the following expression:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where  $k_2$  is the pseudo-second order rate constant ( $\text{g}/\text{mg}\cdot\text{min}$ ) and  $h = k_2 q_e^2$ , is the initial adsorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ ). The pseudo-second order kinetic parameters can be calculated from the slope and intercept of the plot  $t/q_t$  versus time (Fig. 2 (c)) and the values were listed in Table 2. The pseudo-second order kinetic plots shows a higher coefficient of determination values ( $R^2$ ) and better conformity with the pseudo-second order kinetic model. The  $R^2$  values for the pseudo-second order kinetic model are greater than 0.996 at optimum conditions. The calculated values of  $q_e$  from the pseudo-second order kinetic model are much closer to the

**Table 2.** Comparison of maximum monolayer adsorption capacity of SMSP for Zn(II) ions with other adsorbents

Adsorbents	$q_m$ (mg/g)	Reference
Maize husk (EDTA modified)	769.23	12
Sulphuric acid treated cashew nut shell	455.7	5
Surface modified <i>Strychnos potatorum</i> seeds	98.75	This study
<i>Azadirachta indica</i> bark	33.49	13
Activated carbon from bagasse	31.11	14
Cashew nut shell	24.98	15
Xanthate modified magnetic chitosan	20.8	16
Lignocellulosic substrate	16.02	17
Rice bran	14.17	18
Physic seed hull	12.29	19
Lignin	11.25	20
Coir	8.60	21
Bagasse fly ash	7.03	22
Cork biomass	6.80	23
Banana peel	5.80	24
Orange peel	5.25	24

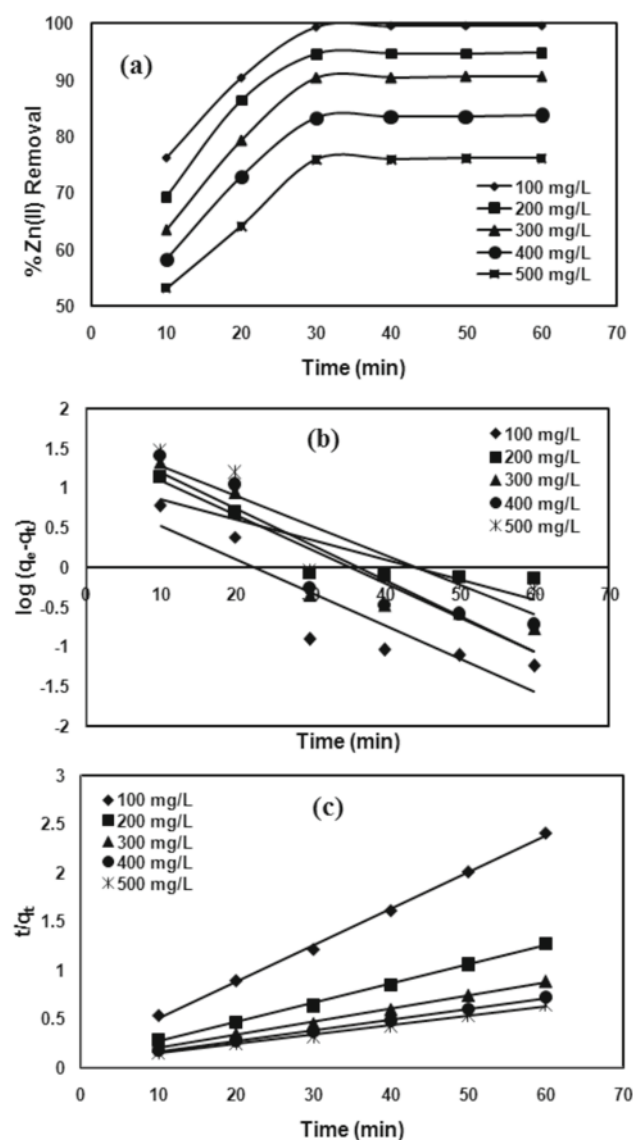
experimental  $q_e$  values than that of pseudo-first order kinetic model. So the adsorption of Zn(II) ions onto the SMSP in this study was better fitted to the pseudo-second order kinetic model.

### Adsorption mechanism

The intraparticle diffusion model<sup>14</sup>, Boyd kinetic model<sup>15</sup> and shrinking core model<sup>16</sup> were plotted in order to verify the influence of mass transfer resistance on the adsorption of Zn(II) ions onto the SMSP. The possibility of the particle diffusion resistance affects the adsorption of Zn(II) ions onto the SMSP was explored using the intraparticle diffusion model as follows:

$$q_t = k_p t^{1/2} + C \quad (9)$$

where  $q_t$  is the amount of Zn(II) ions adsorbed onto the SMSP at time  $t$  (mg/g),  $k_p$  is the intraparticle diffusion constant ( $\text{mg/g min}^{0.5}$ ),  $t$  is the time (min) and  $C$  is the intercept. The values of  $k_p$  and  $C$  were calculated from the slope and intercept of the plot of  $q_t$  versus square root of time (Fig. 3 (a)) and the values are listed in Table 3. If this plot passes through the origin then the intraparticle diffusion is the rate controlling step. But, the linear portion of the plot did not pass through the origin. This deviation from the origin may be due to the difference in rate of mass transfer in the initial and final stages of adsorption. This is the indicative of some degree of film diffusion controls the adsorption process. This was further confirming that the intraparticle diffusion is not only the rate-limiting step but also may be the rate of adsorption or all may be playing simultaneously. The influence of mass transfer in the removal of Zn(II) ions using SMSP was also checked with the help of Boyd kinetic plot.



**Figure 3.** Adsorption kinetics for the removal of Zn(II) ions by SMSP (Zn(II) ions concentration = 100–500 mg/L, pH = 5.0, SMSP dose = 0.4 g, volume of sample = 100 mL, and temperature 30°C)

**Table 3.** Pseudo-first order and pseudo-second order kinetic constants for Zn(II) ions adsorption onto the SMSP

Kinetic models	Parameters	Concentration of Zn(II) ions solution (mg/L)				
		100	200	300	400	500
Pseudo-first order equation	$k_1$ (min <sup>-1</sup> )	0.094	0.058	0.099	0.104	0.085
	$q_{e,cal}$ (mg/g)	8.709	12.882	33.266	43.853	43.551
	$R^2$	0.816	0.744	0.838	0.843	0.800
Pseudo-second order equation	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	0.0113	0.0051	0.0032	0.0024	0.0016
	$q_{e,cal}$ (mg/g)	27.027	52.632	71.429	90.909	111.111
	$h$ (mg g <sup>-1</sup> min <sup>-1</sup> )	8.264	14.084	16.129	19.608	20.408
	$q_{e,exp}$ (mg/g)	24.985	48.122	68.15	83.88	95.75
	$R^2$	0.998	0.997	0.996	0.996	0.996

**Table 4.** Intraparticle diffusion, Boyd kinetic and SCM Model for Zn(II) ions adsorption onto the SMSP

Concentration of Zn(II) ions solution (mg/L)	Intraparticle diffusion model			Boyd kinetic model			SCM model	
	$k_p$ (mg/g·min <sup>1/2</sup> )	C	$R^2$	B	$D_i$ ( $\times 10^{-12}$ m <sup>2</sup> /s)	$R^2$	$D$ ( $\times 10^{-9}$ m <sup>2</sup> /s)	$R^2$
100	1.230	16.52	0.771	0.096	5.078	0.816	3.934	0.773
200	2.604	29.67	0.774	0.058	3.068	0.744	5.582	0.838
300	4.322	38.38	0.780	0.099	5.237	0.838	5.268	0.828
400	5.398	46.73	0.783	0.103	5.449	0.843	4.859	0.803
500	6.345	51.57	0.803	0.085	4.497	0.800	3.667	0.784

The adsorption kinetic data was applied to the Boyd kinetic plot to know the actual slowest step in the adsorption process and the results were presented in the Fig. 3 (b). The Boyd kinetic equation is given by the following relationship:

$$F = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \exp(-Bt) \quad (10)$$

The Eq.(10) can be modified into the following form:

$$Bt = -0.4977 - \ln(1-F) \quad (11)$$

where  $q_e$  is the amount of Zn(II) ions adsorbed onto the SMSP at equilibrium (mg/g),  $q_t$  is the amount of Zn(II) ions adsorbed onto the SMSP at time  $t$ ,  $F$  is the fraction of Zn(II) ions adsorbed at any time  $t$ , and  $Bt$  is a mathematical function of  $F$ . If the plot of  $[-0.4977 - \ln(1-F)]$  versus time is linear and pass through the origin then the actual slowest step or rate controlling step in the adsorption of Zn(II) ions onto the SMSP is the intraparticle diffusion. But, it can be seen from the Fig. 3(b) that the plots were appeared to be linear but did not pass through the origin. This suggests that the adsorption of Zn(II) ions onto the SMSP was actually controlled by film diffusion. The effective diffusion coefficient,  $D_i$  (m<sup>2</sup>/s) values was estimated using the following relationship and the values are listed in Table 3:

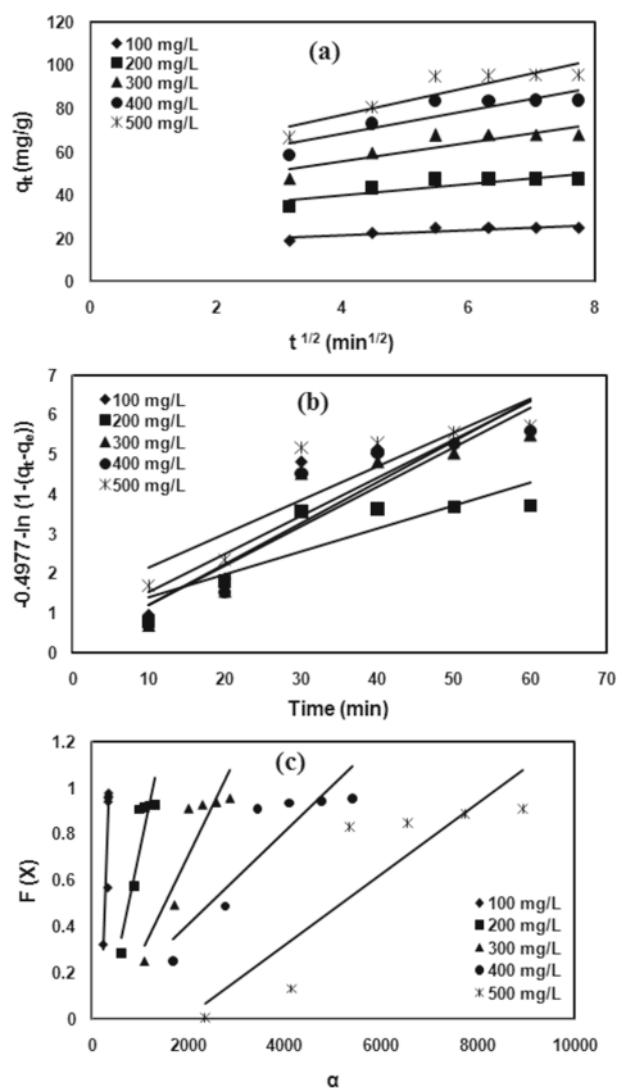
$$B = \frac{\pi^2 D_i}{r^2} \quad (12)$$

where  $D_i$  is the effective diffusion coefficient and  $r$  is the radius of the SMSP particles.

The adsorption kinetics data was further applied to the shrinking core model and the results were presented in Fig. 3 (c). The overall rate for the adsorption of adsorbate onto the adsorbent (diffusion plus reaction) depends primarily on the diffusivity. The kinetic models have been developed to calculate the mass transfer characteristic parameters in the adsorption process. This kinetic model was applied to the fluid-particle chemical reactions by Levenspiel<sup>16</sup>. If the process is controlled by the film diffusion then the extent of the adsorption process is a function of time and it is given by the following expression:

$$X = \frac{3D}{\delta RC} \alpha \quad (13)$$

If the film diffusion is the rate controlling step in the adsorption process then the plot of  $X$  versus  $\alpha$  should



**Figure 4.** Adsorption mechanism for the removal of Zn(II) ions by SMSP (Zn(II) ions concentration = 100–500 mg/L, pH = 5.0, SMSP dose = 0.4 g, volume of sample = 100 mL, and temperature 30°C)

produce a straight-line. If the process is controlled by the diffusion through the reacted shell (particle diffusion control) then the kinetic model is given by the following expression:

$$F(X) = 1 - 3(1-X)^{\frac{2}{3}} + 2(1-X) = \frac{6D}{R^2 C^0} \alpha \quad (14)$$

For the particle diffusion control, a plot of  $F(X)$  versus  $\alpha$  gave a straight-line (Fig. 3 (c)) and the diffusivity values can be calculated from the following expression and the values are listed in Table 3:

$$D = (\text{Slope}) \frac{C^0 R^2}{6} \quad (15)$$

where

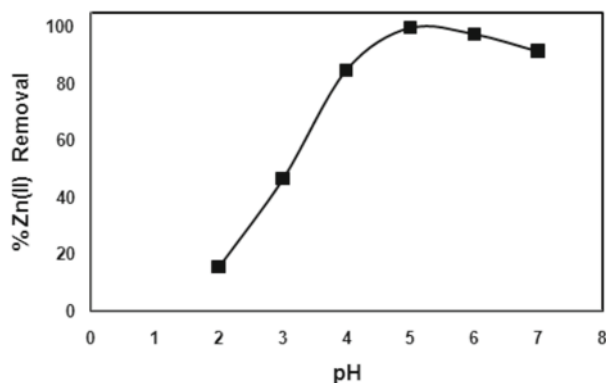
$$X \text{ is the extent of reaction} = \frac{(C_0 - C)}{(C_0 - C_{eq})} \quad (16)$$

$$\alpha = \int_0^t C \, dt \quad (17)$$

where  $C_0$  is the initial Zn(II) ions concentration (mg/L),  $C_0$  is the average Zn(II) ions binding site density of the SMSP (mg/L),  $C$  is the final Zn(II) ions concentration (mg/L),  $C_{eq}$  is the concentration of Zn(II) ions at equilibrium (mg/L),  $\delta$  is the film thickness (mm),  $D$  is the diffusion coefficient ( $\text{m}^2/\text{s}$ ) and  $R$  is the radius of the adsorbent particle (m).

### Effect of solution pH

One of the most important operating parameters which affect the adsorption of metal ions onto the adsorbent surface is acidity of the solution. The effect of solution pH on the adsorption of Zn(II) ions onto the SMSP was studied at pH 2.0–7.0 for initial Zn(II) ion concentration of 100 mg/L solution. The results of the pH studies were presented in Fig. 5. It was observed from the Fig. 5, the percentage removal of Zn(II) ions was increased with the increase in solution pH and it reaches the maximum value of 99.444% at a pH of 5.0 and then declined with further increase in pH. At low pH, the adsorption of Zn(II) ions is very low because the large quantity of hydronium ions competes with the Zn(II) ions to the adsorption sites of the adsorbent. The decrease in the removal of Zn(II) ions at higher



**Figure 5.** Effect of solution pH on the adsorption of Zn(II) ions onto the SMSP (Zn(II) ions concentration = 100 mg/L, SMSP dose = 0.4 g, equilibrium time = 30 min, volume of sample = 100 mL, and temperature 30°C)

pH may be due to the formation of insoluble hydroxide precipitation from solution which makes the true Zn(II) ions adsorption studies impossible. From the results, it was observed that the optimum solution pH for the present adsorption system was 5.0.

### Batch desorption experiments

Both incineration and land disposal methods are the most important method for the disposal of the spent adsorbent. However, both of these methods produce either direct or indirect impacts over the environment. The application of the thermal activation method to regenerate the spent adsorbent would require more energy and 5–10% adsorbent loss in each cycle. If the regeneration of Zn(II) ions from the spent SMSP is possible, it would not only protect the environment, but also help recycle the Zn(II) ions and SMSP, and hence, contribute to the economy of wastewater treatment. Desorption studies help in elucidating the adsorption mechanism of the removal of Zn(II) ions from the aqueous solution using the SMSP and the recovery of Zn(II) ions from the spent SMSP and the aqueous solution. Hence, desorption studies were tried through chemical regeneration for the spent SMSP. The results of the desorption studies indicates that the percentage recovery of Zn(II) ions was increased with the increase in the concentration of HCl solution from 0.1 M to 0.35 M and it reaches a constant value (93.58%) with the 0.30 M HCl for spent SMSP.

### CONCLUSIONS

The adsorption experimental investigation concluded that the surface modified *Strychnos potatorum* seeds (SMSP) could be used as an adsorbent for the removal of Zn(II) ions from aqueous environment. The adsorption equilibrium data best fitted the Freundlich adsorption isotherm model. The maximum monolayer adsorption capacity of the SMSP for the removal of Zn(II) ions was found to be 98.75 mg/g at an optimum pH of 5.0. The adsorption kinetics revealed that the adsorption process followed the pseudo-second order kinetic model. The particle diffusion and film diffusion played an important role in controlling the adsorption of Zn(II) ions onto the SMSP and this was identified by fitting the adsorption kinetic data with the intraparticle diffusion, Boyd kinetic and Shrinking Core Models. The reusability of the SMSP was found to be good without any considerable loss in adsorption capacity during the cycles of desorption. From the results, it was observed that the SMSP can be used as an alternative adsorbent for the removal of Zn(II) ions from the aqueous solution.

### Acknowledgements

The author is very grateful for the financial support from the SSN Trust, Chennai.

### LITERATURE CITED

1. Bureau of Indian Standards (BIS). (1994). Methods of sampling and test (physical and chemical) for water and waste water: Part 49 Zinc, IS No. 3025 (Part 49).
2. Nuhoglu, Y. & Malkoc, E. (2009). Thermodynamic and kinetic studies for environmentally friendly Ni(II) biosorption

using waste pomace of olive oil factory. *Bioresour. Technol.* 100, 2375–2380. DOI: 10.1016/j.biortech.2008.11.016.

3. Ofomaja, A.E., Unuabonah, E.I. & Oladoja, N.A. (2010). Competitive modeling for the biosorptive removal of copper and lead ions from aqueous solution by *Mansonia* wood sawdust. *Bioresour. Technol.* 101, 3844–3852. DOI: 10.1016/j.biortech.2009.10.064.

4. SenthilKumar, P., Ramalingam, S., Sathyaselvabala, V., Kirupha, S.D. & Sivanesan, S. (2011). Removal of copper(II) ions from aqueous solution by adsorption using cashew nut shell. *Desalination*. 266, 63–71. DOI: 10.1016/j.desal.2010.08.003.

5. Kumar, P.S., Ramalingam, S., Abhinaya, R.V., Kirupha, S.D., Murugesan, A. & Sivanesan, S. (2012). Adsorption of metal ions onto the chemically modified agricultural waste. *CLEAN – Water, Air, Soil*. 40 (2), 188–197. DOI: 10.1002/clen.201100118.

6. Kumar, P.S., Ramalingam, S., Sathyaselvabala, V., Kirupha, S.D., Murugesan, A. & Sivanesan, S. (2012). Removal of Cadmium(II) from aqueous solution by agricultural waste cashew nut shell. *Korean J. Chem. Eng.* 29 (6), 756–768. DOI: 10.1007/s11814-011-0259-2.

7. Kumar, P.S., Gayathri, R., Senthamarai, C., Priyadharshini, M., Fernando, P.S.A., Srinath, R., & Kumar, V.V. (2012). Kinetics, mechanism, isotherm and thermodynamic analysis of adsorption of cadmium ions by surface-modified *Strychnos potatorum* seeds. *Korean J. Chem. Eng.* 29 (12), 1752–1760. DOI: 10.1007/s11814-012-0077-1.

8. Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Ame. Chem. Soc.* 40, 1361–1403.

9. Freundlich, H.M.F. (1906). Over the adsorption in solution. *J. Phy. Chem.* 57, 385–470.

10. McKay, G., Otterburn, M.S. & Sweetney, A.G. (1981). The removal of colour from effluent using various adsorbents, III Silica rate process. *Water Res.* 14, 14–20. DOI: 10.1016/0043-1354(80)90037-8.

11. Eagleton, K.R., Acrivers, L.C. & Vermeulen, T. (1966). Pore and solid diffusion kinetics in fixed adsorption constant pattern conditions. *Ind. Eng. Chem. Res.* 5, 212–223. DOI: 10.1021/i160018a011.

12. Igwe, J.C. & Abia, A.A. (2007). Equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from waste water using unmodified and EDTA-modified maize husk. *Electron. J. Biotechnol.* 10, 536–548. DOI: 10.2225/vol10-issue4-fulltext-15.

13. King, P., Anuradha, K., Lahari, S.B., Kumar, Y.P. & Prasad, V.S.R.K. (2008). Biosorption of Zinc From Aqueous Solution Using *Azadirachta indica* bark: Equilibrium and kinetic Studies. *J. Hazard. Mater.* 152, 324–329. DOI: 10.1016/j.jhazmat.2007.06.101.

14. Mohan, D. & Singh, K.P. (2002). Single-and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse – an agricultural waste. *Water Res.* 36, 2304–2318. DOI: 10.1016/S0043-1354(01)00447-X.

15. SenthilKumar, P., Ramalingam, S., Abhinaya, R.V., Kirupha, S.D., Vidhyadevi, T. & Sivanesan, S. (2012). Adsorption equilibrium, thermodynamics, kinetics, mechanism and process design of Zinc(II) ions onto cashew nut shell. *Can. J. Chem. Eng.* 90, 973–982. DOI: 10.1002/cjce.20588.

16. Zhu, Y., Hu, J. & Wang, J. (2012). Competitive adsorption of Pb(II), Cu(II) and Zn(II) onto xanthate-modified magnetic chitosan. *J. Hazard. Mater.* 221–222, 155–161. DOI: 10.1016/j.jhazmat.2012.04.026.

17. Dupont, L., Bounanda, J., Dumonceau, J. & Aplincourt, M. (2005). Biosorption of Cu(II) and Zn(II) onto a Lignocellulosic substrate extracted from wheat bran, *Environ. Chem. Lett.* 2, 165–168. DOI: 10.1007/s10311-004-0095-2.

18. Wang, X., Qin, Y. & Li, Z. (2006). Biosorption of zinc from aqueous solutions by rice bran: Kinetics and equilibrium studies, *Sep. Sci. Tech.* 41, 741–756. DOI: 10.1080/01496390500527951.

19. Mohammad, M., Maitra, S., Ahmad, N., Bustam, A., Sen, T.K. & Dutta, B.K. (2010). Metal ion removal from aqueous solution using physic seed hull. *J. Hazard. Mater.* 179, 363–372. DOI: 10.1016/j.jhazmat.2010.03.014.

20. Guo, X.Y., Zhang, A.Z. & Shan, X.Q. (2008). Adsorption of metal ions on lignin. *J. Hazard. Mater.* 151, 134–142. DOI: 10.1016/j.jhazmat.2007.05.065.

21. Conrad, K. & Hansen, H.C.B. (2007). Sorption of zinc and lead on coir. *Bioresour. Technol.* 98, 89–97. DOI: 10.1016/j.biortech.2005.11.018.

22. Srivastava, V.C., Mall, I.D. & Mishra, I.M. Modelling individual and competitive adsorption onto cadmium (II) and zinc (II) metal ions from aqueous solution onto bagasse fly ash, *Sep. Sci. Tech.* 41(12), 2685–2710. DOI: 10.1080/01496390600725687.

23. Chubar, N., Carvalho, J.M.R. & Correia, M.J.N. (2003). Cork biomass as biosorbent for Cu(II), Zn(II), Ni(II). *Colloids Surf. A Physicochem. Eng. Aspects.* 230, 57–65. DOI: 10.1016/j.colsurfa.2003.09.014.

24. Annadurai, G., Jung, R.S. & Lee, D.J. (2003). Adsorption of heavy metals from water using banana and orange peels, *Water Sci. Tech.* 47, 185–190.

25. Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetensk. Handl.* 24, 1–39.

26. Ho, Y.S. & McKay, G. (1999). Pseudo-second order model for sorption processes. *Proc. Biochem.* 34, 451–465.

27. Weber, W.J. & Morris, J.C. (1963). Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* 89, 31–60.

28. Boyd, G.E., Adamson, A.W. & Myers, L.S. (1947). The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics. *J. Ame. Chem. Soc.* 69, 2836–2848.

29. Levenspiel, O. (1999). Chemical reaction engineering, 3<sup>rd</sup> Edition, John Wiley & Sons.

30. Lewandowski, Z. & Roe, F. (1994). Communication to the editor: diffusivity of Cu<sup>2+</sup> in calcium alginate gel beads. *Biotech. Bioeng.* 43, 186–187.

31. Veglio, F., Beolchini, F. & Gasbarro, A. (1997). Biosorption of toxic metals: an equilibrium study using free cells of *Arthrobacter* sp. *Proc. Biochem.* 32, 99–105. DOI: 10.1016/S0032-9592(96)00047-7.