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# Biosorption of lead(II) ions onto nano-sized chitosan particle blended polyvinyl alcohol (PVA): adsorption isotherms, kinetics and equilibrium studies

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## ABSTRACT

Lead(II) ion is one of the most toxic heavy metal present in the industrial effluents that pose many health hazards to the living environment. The current investigation aimed at synthesizing nano-sized chitosan particles and then blending them with polyvinyl alcohol (PVA) to produce a stable chitosan/PVA composite membrane. This composite proved to be a promising adsorbent for the removal of lead(II) ions from the aqueous solution. The prepared nanoparticles of chitosan were characterized using Transmission electron microscope analysis. The morphological nature and the attachment of lead ions onto the adsorbent were studied using scanning electron microscope analysis. The adsorption ability of chitosan/PVA blend was optimized by varying physical parameters such as pH, adsorbent dose, adsorbate concentration, contact time, and temperature. The maximum adsorption of 96.1% was regarded for an initial concentration of 10 mg/L, adsorbent dose of 0.6 g/100 mL at 30˚C. The adsorption kinetics were studied with pseudo-first order, pseudo-second order, Weber and Morris intraparticle diffusion and Boyd kinetic models and was found that the system better fitted the pseudo-second order kinetic model. The desorption of lead(II) ions was done effectively using HCl solution, thereby proving that chitosan/PVA blend can be regenerated and reused effectively for further process of removal.

*Keywords:* Chitosan; PVA; TEM; SEM; Lead(II) ions

## 1. Introduction

Lead ($Pb^{2+}$), a cation, is a prime constituent of most of the industrial effluents such as mining, smelting and coal combustion, lead-based painting and lead containing pipes in water supply systems, paper and pulp refineries, printing, paints and pigments, explosive manufacturing, storage batteries, alloy and steel industries [1,2]. The maximum permissible limit of lead in the water used for drinking and domesticating

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purpose is 0.01 mg/L as suggested by Bureau of Indian Standards, BIS [3]. This becomes the acceptable "safe" level of lead(II) ions in water beyond which, the water becomes unfit for human use and consumption, and is potential enough to lead health problems and epidemics leading to kidney failure, neuronal disorders, and reproductive infertility [4,5]. This urges for the proper treatment of industrial effluents before supplying domestic use, to provide the environment as well as the human community for encountering serious consequences in terms of pollution and health, respectively [6,7]. The advancement in modern technology has opened up to a wide range of techniques for the treatment of industrial effluents [8]. Most popular ones being chemical coagulants, ion exchangers, membrane filters, reverse osmosis, precipitation, and adsorption, among which our choice of interest is adsorption [9]. Adsorption is the most convenient technique that can be adopted due to its operational simplicity, cost efficiency, affordability, etc. [8,10].

Chitosan is a deacetylated derivative of chitin, the natural, most abundantly available polysaccharide, which is a polymer of N-acetyl glucosamine and glucosamine units [11,12]. Chitosan has multiple valuable properties such as non-toxic [13], biodegradable [14], biocompatible [15,16], soluble in dilute acids [17], and also chelates metal ions [15]. Polyvinyl alcohol (PVA) is a non-toxic, biodegradable as well as a biocompatible polymer that also had a number of useful property such as polar and hydrophilicity, enhanced tensile strength, film-forming ability, and good physical strength [18–22]. PVA has been commonly used in the membrane preparation as natural/synthetic blends with the other class of materials. Polymeric blends are opening up a variety of applications in the field of adsorption. Among which chitosan forms a firm and uniformly distributed membrane with PVA, which possess the property to adsorb metal ions. Blends of chitosan/PVA introduced the new class of membrane possessing improved tensile strength, mechanical, and physical properties [23].

This study includes blending of chitosan nanoparticles with PVA to form a uniform membrane that is employed as an adsorbent for the removal of lead(II) ions. The membrane was characterized using analytical techniques such as scanning electron microscope (SEM), transmission electron microscope (TEM), and fourier transform infrared spectroscopy. The different physical parameters were varied and optimized that includes pH, adsorption dose, initial concentration, temperature, and contact time. The pseudo-first order, pseudo-second order, intraparticle and Boyd kinetic models, and adsorption isotherms were analyzed and the different thermodynamic constants were determined. Finally, the desorption process was carried out and studied for the recovery of the adsorbent.

## 2. Experimental

### 2.1. Preparation of adsorbent

A total of Two gram of chitosan was dissolved in 100 mL of 4% acetic acid solution and stirred at constant speed for 20 min [24]. Then, 20 mL of 3% trisodium polyphosphate solution was added to the chitosan acetic acid solution dropwise (in the ratio 5:2) as again stirred at constant speed for 30 min. The solution was then centrifuged at a maximum speed of 10,000 rpm at 30℃ for 30 min. The nanoparticles of chitosan were formed as pellet, which was collected and stored at 4℃ for an hour [24]. The formation of chitosan nanoparticles was then confirmed using TEM. The chitosan nanoparticles were then blended with PVA in the ratio of 1:3 using glutaraldehyde as a cross-linking agent. The solution was left undisturbed for 24 h under room temperature to facilitate the formation of a smooth membrane. Once formed, the membrane was dried and powdered by crushing to the required size to be used as an effective adsorbent for our further studies.

### 2.2. Preparation of lead(II) solution

Appropriate amount of lead acetate salt was dissolved in double-distilled water to prepare a stock solution of lead ions of 100 mg/L concentration. The working solutions of varying concentration from 10 to 50 mg/L were prepared using the stock solution. Throughout the study, the pH values of different working solutions were adjusted to the required values using 0.1 M NaOH or 0.1 M HCl.

### 2.3. Batch adsorption experiments

The batch adsorption experiments were carried out by varying and optimizing the physical parameters such as pH, adsorbent dose, initial concentration, contact time, and temperature. Erlenmeyer flasks containing 100 mL of lead(II) solution each were kept in a shaker by varying the initial concentration (10–50 mg/L) and contact time (10–80 min), pH (2–8), temperature (30–60℃) for a standard adsorbent dose of 20 mg/L. The mixture was then filtered as the final concentration of lead(II) ions from the filtrate was determined at 217 nm using atomic absorption spectroscopy (AAS). Each experiment was carried out at two trials and the means of the two trials were considered as optimum value. The % removal of lead(II) ions in each case was determined using the following formula:

$$\% R = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$C_0$ is the initial concentration of lead(II) ions (mg/L), and $C_e$ is the final concentration of lead(II) ions (mg/L).

To carry out the kinetic and equilibrium studies, batch adsorption experiments were carried out by treating 100 mL of lead(II) ion solution with 0.6 g of chitosan–PVA blend adsorbent, by varying the concentration of the solution between 10 and 50 mg/L. The equilibrium concentrations of the solution were determined using AAS at 217 nm as the value of $q_e$ was calculated using the following formula:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

$q_e$ is the amount of lead(II) ions adsorbed at equilibrium (mg/g), $V$ is the volume of ions (L), $C_0$ is the initial concentration of lead(II) ions (mg/L), and $m$ is the mass of adsorbent (g). The desorption studies were also carried out for varying HCl concentration from 0.05 M to 0.2 M to find the percentage recovery of lead(II) ions.

### 2.4. Desorption studies

Desorption studies were carried out for the recovery of lead(II) ions onto chitosan/PVA blend using different concentrations of HCl varying from 0.05 M to 0.2 M. The spent chitosan/PVA blend obtained from five different concentrations ranging from 10 to 50 mg/L of lead(II) ions solution was suspended in 100 mL of HCl solution and kept in a rotary shaker at 150 rpm, 30°C for an hour. Then, the adsorbent was separated out, and the residual lead(II) ion solution was taken to study the concentration of lead(II) ions present using AAS, after the process of desorption.

## 3. Results and discussion

### 3.1. Characterization of adsorbent

The TEM analysis was performed using computer aided tEM of Philips make. Fig. 1 shows F1 typical bright-field TEM image of chitosan nanoparticles with the size found to be 152.10 nm. The chitosan/PVA composite was characterized by analyzing the composite membrane and examining it under SEM. Figs. 2(a) and 2(b) depict the morphological nature of chitosan/PVA membrane before and after the adsorption of lead(II) ions, respectively. Under microscopic examination, chitosan/PVA (Fig. 2(a)) blend shows a rough non-uniform surface with highly shrunken pores. In addition, the image clearly proves that chitosan and PVA have a perfect blend without forming any coagulates. Hence, this membrane acts as a good adsorbent by providing larger surface area and effective binding domains for the adsorption of lead(II) ions. After the adsorption of lead(II) ions onto chitosan/PVA surface (2b), the surface of the adsorbent

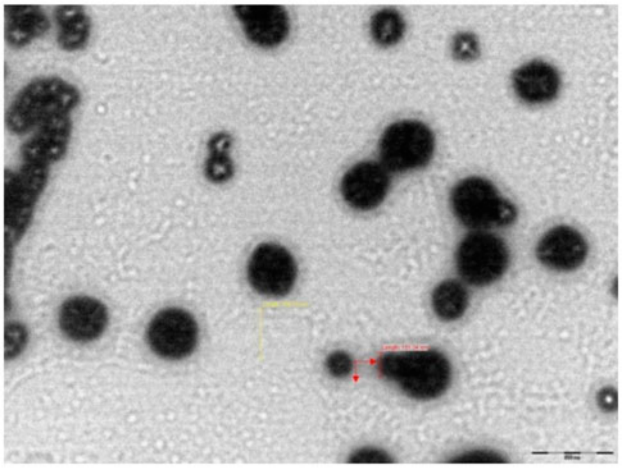

Fig. 1. TEM image of chitosan nanoparticles.

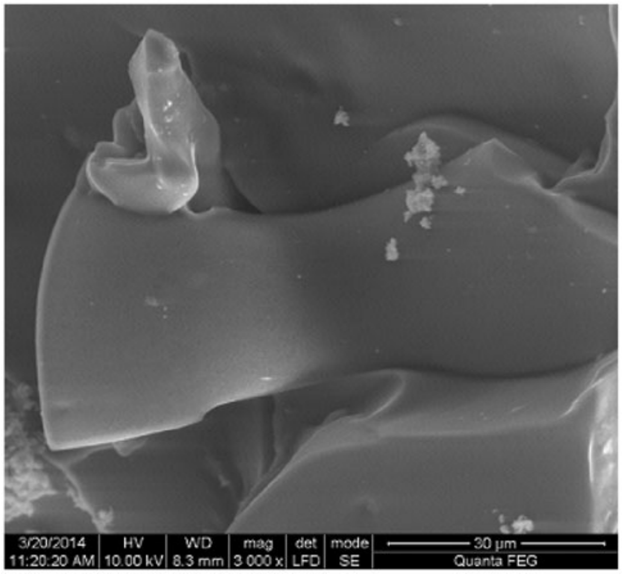

Fig. 2a. SEM micrograph of chitosan-blended PVA before the adsorption of lead(II) ions.

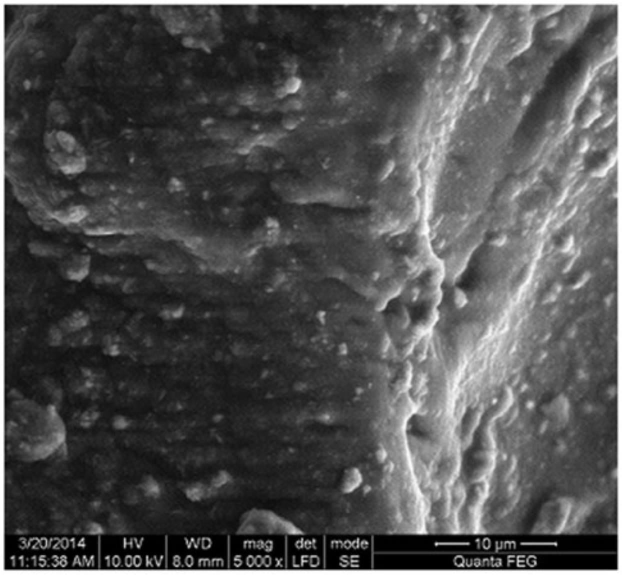

Fig. 2b. SEM micrograph of chitosan-blended PVA after the adsorption of lead(II) ions.

gets filled up with lead(II) ions. This is because of the action of active –$NH_2$ functional groups that are present on the surface of chitosan/PVA blend which helps in strong adsorption of lead(II) ions present in the solution. This is illustrated by the aggregates of lead(II) ions that are clogged onto the membrane as depicted in Fig. 2(b).

### 3.2. *Effect of solution pH*

The solution pH plays an important role in the adsorption of lead(II) ions onto chitosan cross-linked PVA. The pH of the solution was varied from 2 to 8, for an adsorbent dose of 6 g/L. The percentage removal of lead ions against pH was plotted and shown in Fig. 3. The maximum removal of lead ions was attained at a pH of 5 after which there was a decrement in the removal of ions. Henceforth, pH 5 was taken to be optimum for further experimental studies. At the start, when the pH value is low, the decrease in pH value favors the increase in the number of cationic adsorbent sites and reduces the number of anionic adsorption sites. This increases the hydrogen ions concentration in the solution and in turn increases the electrostatic repulsion, and hence, lead is a positively charged ion which does not favor adsorption. As the pH value furthermore increases, the number of anionic adsorption sites on the chitosan/PVA surface increases, which in turn increases the concentration of $OH^-$ ions in the solution, favors the adsorption rate of lead ions on account of the increased electrostatic forces of attraction. But still further, more increase in pH may reduce the rate of adsorption due to the formation of metal hydroxides.

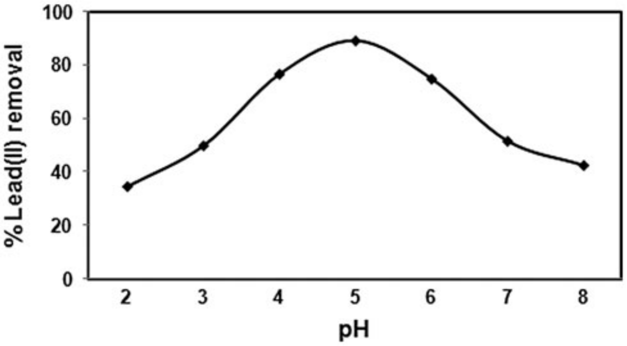

Fig. 3. Effect of pH on lead(II) ions removal by chitosan/PVA blend (lead(II) ion concentration = 10 mg/L, chitosan/PVA blend dose = 6 g/L, equilibrium time = 30 min, volume of sample = 100 mL and temperature = 30℃).

### 3.3. *Effect of adsorbent dose*

The effect of adsorbent dose on the adsorption of lead(II) ions was studied and analyzed by maintaining constant values of all other working parameters (pH 5, temperature 30℃, volume of the solution = 100 mL) and varying only the adsorbent dose from 0.2 to 1 g/100 mL. The result was shown in Fig. 4, and the experimental results reveal that the percentage removal of lead(II) ions increases linearly with the increase in the dosage of adsorbent loading up to a threshold of 0.6 g/100 mL accounting for 89.55% removal of lead ions from the solution. There is no significant change in percentage removal of lead ions above the threshold value. This may be accounted by

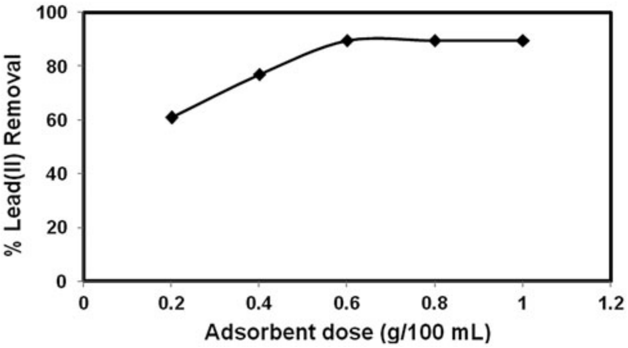

Fig. 4. Effect of adsorbent dose on lead(II) ions removal by chitosan/PVA blend (lead(II) ion concentration = 10 mg/L, volume of sample = 100 mL, pH 5.0, equilibrium time = 30 min and temperature = 30℃).

the surface saturation of adsorbent and the decreased affinity of the adsorbent for the lead(II) ions in the solution. Hence, the adsorbent dose of 6 g/L was taken to be optimum and kept constant for further studies.

### 3.4. *Effect of contact time on lead(II) ion adsorption*

The contact time is an important factor governing the adsorption process since it directly influences the equilibrium stage of the process. The effect of contact time was investigated by keeping operating parameters constant (adsorbent dose 6 g/L, pH 5, temperature 30℃) and by only varying the contact time, and the results were depicted in Fig. 5. It was observed that there was an initial steep increase in the % removal of lead(II) ions till the equilibrium state was attained. But in due course of time, after which there was not any significant variation in the removal of ions. Therefore, the contact time of 40 min was optimized for further experimental studies. It was found that the maximum removal of lead(II) ions was reached at adsorbate concentration 20 mg/L for a contact time of 40 min.

The effect of contact time formed the basis for deriving the kinetic data and tests the different adsorption kinetic models such as pseudo-first order and pseudo-second order.

The Lagergren's pseudo-first-order kinetic model [25] is expressed in the linear form as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$

And the pseudo-second order-kinetic model [26] takes the linear form as follows:

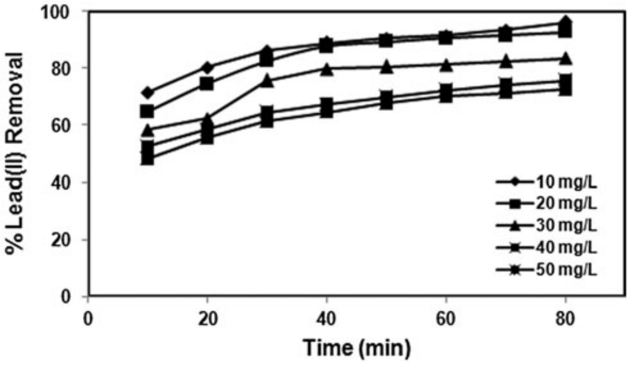

Fig. 5. Effect of contact time on lead(II) ions removal by chitosan/PVA blend (lead(II) ion concentration = 10–50 mg/L, pH 5.0, chitosan/PAN blend dose = 6 g/L, volume of sample = 100 mL, and temperature = 30℃).

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \tag{4}$$

where $q_e$—adsorption capacity at equilibrium (mg/g), $q_t$—adsorption capacity at time $t$ (mg/g), $k_1$—rate constant of pseudo-first-order kinetics (min$^{-1}$), $k_2$—rate constant of pseudo-second order kinetics (g/mg min), $t$—time (min), $h = k_2 q_e^2$ = rate of initial adsorption (mg/g min).

The kinetic parameters, adsorption capacity at equilibrium, and coefficient of determination ($R^2$) values were determined from the slope and intercept of the pseudo-first order (Fig. 6) and pseudo-second order from Fig. 7 and tabulated the results in Table 1. It was observed from the table that the coefficient of determination ($R^2$) attained a higher value for pseudo-second-order kinetic model indicating that pseudo-second-order kinetic theory better elucidates the adsorption kinetics of lead(II) ions onto the chitosan/PVA than the pseudo-first-order kinetic theory. Moreover, the closer agreement of the calculated adsorption

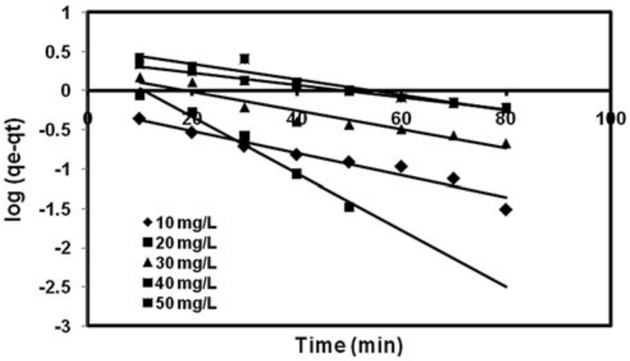

Fig. 6. Pseudo-first-order kinetics for the adsorption of lead(II) ions onto chitosan/PVA blend.

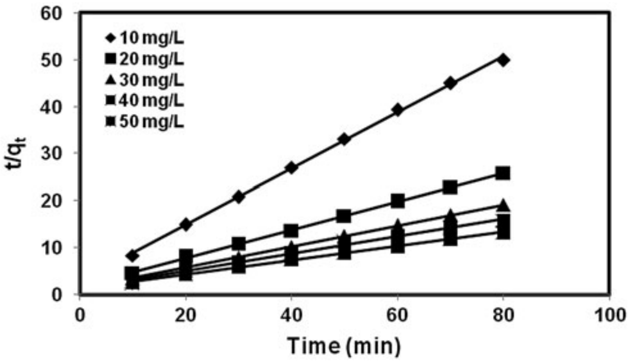

Fig. 7. Pseudo-second-order kinetics for the adsorption of lead(II) ions onto chitosan/PVA blend.

Table 1
Comparison between the pseudo-first-order and pseudo-second-order kinetic models for the adsorption of lead(II) ions onto chitosan-blended polyvinyl alcohol

| | | Concentration of lead(II) ions (mg/L) | | | | |
|---|---|---|---|---|---|---|
| Kinetic model | Parameters | 10 | 20 | 30 | 40 | 50 |
| Pseudo-first-order kinetic equation | $k_1$ (min$^{-1}$) | 0.032 | 0.083 | 0.028 | 0.016 | 0.021 |
| | $q_{e,cal}$ (mg/g) | 0.5902 | 2.443 | 1.698 | 2.455 | 3.499 |
| | $R^2$ | 0.944 | 0.978 | 0.920 | 0.994 | 0.924 |
| Pseudo-second-order kinetic equation | $k_2$ (g/mg min) | 0.123 | 0.051 | 0.034 | 0.024 | 0.019 |
| | $q_{e,cal}$ (mg/g) | 1.672 | 3.322 | 4.525 | 5.464 | 6.622 |
| | $q_{e,exp}$ (mg/g) | 1.633 | 3.013 | 4.392 | 5.639 | 6.658 |
| | $h$ (mg/g min) | 0.345 | 0.561 | 0.694 | 0.714 | 0.818 |
| | $R^2$ | 0.999 | 0.999 | 0.997 | 0.996 | 0.998 |

capacity values ($q_{e,cal}$) from the pseudo-second-order kinetics with the experimentally determined equilibrium adsorption capacity values ($q_{e,exp}$) confirms that the adsorption process of lead(II) ions onto chitosan/PVA follows pseudo-second-order kinetic model.

Since the above two kinetic models did not illustrate the mechanism of adsorption and rate-limiting steps in the adsorption process, the study was extended to deal with Weber and Morris intra-particle diffusion model [27] and Boyd kinetic plot. The solute transfer in a solid–liquid adsorption process is characterized by the film diffusion and/or particle diffusion. The following three events occur consecutively during the adsorption of Pb(II) ions into chitosan–PVA (film diffusion):

(1) Transfer of lead(II) ions from the bulk solution to the exterior surface of chitosan–PVA blend (film diffusion).
(2) Transfers of lead(II) ions into the pores of chitosan–PVA blend (neglecting the insignificant amount of adsorption occurring at the external surface of chitosan–PVA (particle diffusion).
(3) Significant adsorption of lead(II) ions on the interior surface of chitosan–PVA blend.

To study the adsorption mechanism, the kinetic data of adsorption are fitted into intra-particle diffusion equation and Boyd kinetic equation. Fig. 8 shows the results of experimental data fitting in an intra-particle diffusion equation. Weber–Morris intra-particle diffusion equation is given as

$$q_t = k_p t^{1/2} + C \tag{5}$$

where $q_t$ = adsorption equation capacity at time $t$ (mg/g), $k_p$ = rate constant of intra-particle diffusion (mg/g min$^{1/2}$), $t$ is the time (min), and $c$ is the intercept. The intra-particle diffusion becomes the only rate-limiting step if the plot of $q_t$ vs. $t^{1/2}$ passes via origin. Otherwise, the rate-limiting step is governed by the boundary layer control up to some degrees. In such cases, both adsorption and intra-particle diffusion determines the rate-limiting steps. By simultaneous operation, the adsorption of lead(II) ions onto chitosan–PVA blend occurs consecutively by surface adsorption and intra-particle diffusion as indicated by two linear portions in intra-particle diffusion plot. The boundary layer effect is observed by the first linear portion and the intra-particle diffusion is depicted by the second linear portion. All the determined parameters, constants, and $R^2$ values are listed in the Table 2.

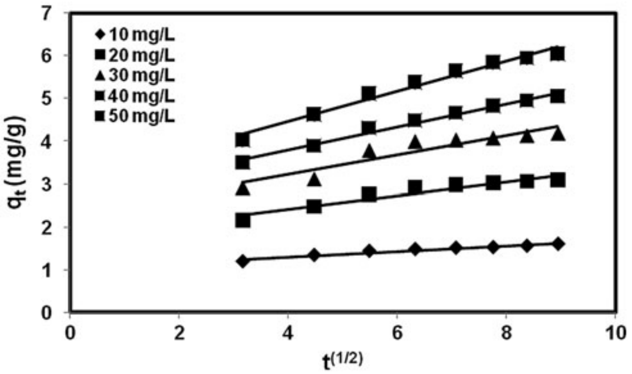

Fig. 8. Intraparticle diffusion model for the adsorption of lead(II) ions onto chitosan/PVA blend.

### 3.5. Boyd kinetic model

The Boyd kinetic plot was used to validate the adsorption kinetic data to identify the actual slowest step in the adsorption of lead(II) ions onto chitosan/

Table 2
Intraparticle diffusion model results obtained for the adsorption of lead(II) ions onto chitosan-blended polyvinyl alcohol

| Concentration of lead(II) ions solution (mg/L) | Parameters | | |
|---|---|---|---|
| | $K_p$ (mg/g min$^{1/2}$) | $C$ | $R^2$ |
| 10 | 0.064 | 1.038 | 0.944 |
| 20 | 0.158 | 1.788 | 0.913 |
| 30 | 0.227 | 2.309 | 0.872 |
| 40 | 0.268 | 2.726 | 0.985 |
| 50 | 0.352 | 3.060 | 0.974 |

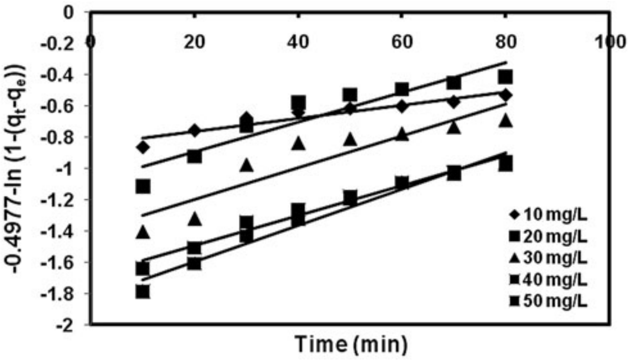

Fig. 9. Boyd kinetic model for the adsorption of lead(II) ions onto chitosan/PVA blend.

PVA. The plot was shown in Fig. 9, and the results were shown in Table 3. The Boyd kinetic equation is as follows:

$$F = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} e^{(-Bt)} \tag{6}$$

where, the above equation can be rearranged in the following form:

$$Bt = -0.4977 - \ln(1 - F) \tag{7}$$

where $q_e$ = equilibrium adsorption capacity (mg/g), $q_t$ is the adsorption capacity at any time (mg/g), $F$ is the fraction of lead(II) ions adsorbed at anytime ($t$), $Bt$—mathematical function of $F$. If the Boyd kinetics plot of "$Bt$ vs. $t$" takes a linear form passing through the origin, it indicates that particle diffusion is the actual slowest step in the adsorption of lead(II) ions onto the chitosan–PVA blend. As depicted in Fig. 9, the Boyd kinetic plot for our experimental system is linear but does not pass via origin, indicating that the adsorption of lead(II) ions onto chitosan/PVA is majorly controlled by film diffusion. The $B$ values were obtained from the plot, which was used to determine the effective diffusion coefficient $D_i$ (m$^2$/s), using the following equation and shown in Table 3.

$$B = \frac{\pi^2 D_i}{r^2} \tag{8}$$

where $D_i$ is the effective diffusion coefficients of lead ions into chitosan/PVA surface, and $r$ is the radius of chitosan/PVA particle.

### *3.6. Effect of initial lead ion concentration on Pb(II) adsorption and adsorption isotherms*

Fig. 10 illustrates the effect of initial concentration of lead(II) ions (10–50 mg/L) on its removal. From the above figure, we can observe that there is a decrease

Table 3
Boyd kinetic model results obtained for the adsorption of lead(II) ions onto chitosan-blended polyvinyl alcohol

| Concentration of lead(II) ions solution (mg/L) | Parameters | | |
|---|---|---|---|
| | $B$ | $D_i \times 10^{-13}$ (m$^2$/s) | $R^2$ |
| 10 | 0.004 | 21.183 | 0.902 |
| 20 | 0.009 | 47.666 | 0.878 |
| 30 | 0.010 | 52.959 | 0.836 |
| 40 | 0.009 | 47.666 | 0.975 |
| 50 | 0.011 | 58.254 | 0.965 |

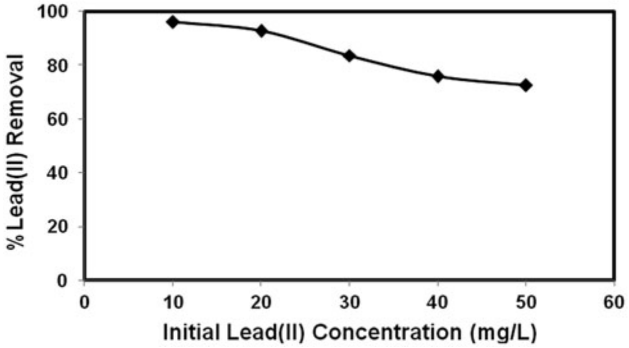

Fig. 10. Effect of initial lead(II) ion concentration on lead (II) ions removal by chitosan/PVA blend (lead(II) ion concentration = 10–50 mg/L, chitosan/PAN blend = 6 g/L, volume of sample = 100 mL, pH 5.0, equilibrium time = 30 min and temperature = 30˚C).

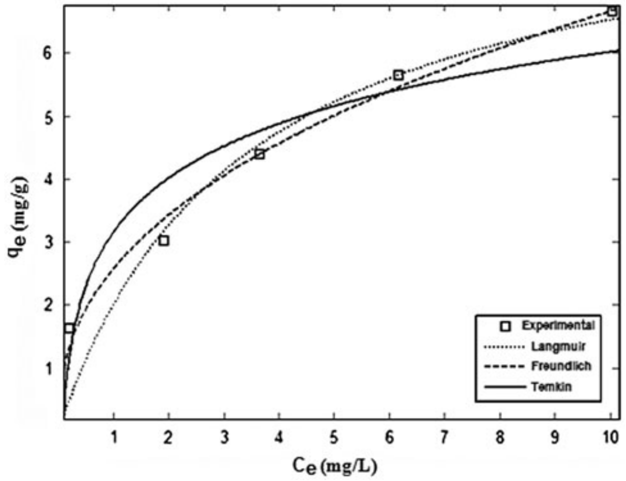

Fig. 11. Adsorption isotherms pH 5, chitosan/PVA dose = 0.6 g, volume of sample = 100 mL, lead(II) ion concentration = 10–50 mg/L, equilibrium time = 40 min, temperature = 30˚C.

in the removal of lead(II) ions with the increase in initial concentration. Initially, at lower lead(II) ion concentration, because of lesser number of lead(II) ions available for adsorption, the % removal of lead(II) ions is high (in the solution), as lead(II) ion concentration is increased, more number of lead(II) ions is available for adsorption in the solution, with respect to a fixed amount of chitosan/PVA dose under study. Hence, the % removal of lead(II) ions decreases on increasing its initial concentration on account of saturation of adsorbent.

Adsorption isotherms form the basic evidence for designing and validating the feasibility of an adsorption system. The distribution pattern of lead(II) ions between the lead solution and chitosan/PVA serves as a good indicator of position of equilibrium in the adsorption process which can be illustrated by a series of adsorption isotherm models. The study of effect of initial concentration of lead(II) in the solution serves as a base for dealing with the popular adsorption isotherm models such as Langmuir, Freundlich, and Temkin isotherm models, used to describe the adsorption process and show in Fig. 11 and the values were shown in Table 4.

The Langmuir adsorption isotherm model [28] takes its nonlinear form as follows:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \tag{9}$$

where $q_e$ is the equilibrium adsorption capacity (mg/g), $q_m$ is the maximum monolayer adsorption capacity (mg/g), $k_L$ is Langmuir constant, associated with to the affinity of lead(II) ions to chitosan/PVA (L/mg), $C_e$ is the equilibrium concentration of lead(II) ions solution (mg/L). The significant parameters of Langmuir adsorption isotherm namely the separation factor "$R_L$" can be used for predicting the affinity of

Table 4
Langmuir and Freundlich adsorption isotherm model for the adsorption of lead(II) ions onto chitosan-blended polyvinyl alcohol

| Adsorption isotherm model | Parameters | Values | $R^2$ | Error function | |
|---|---|---|---|---|---|
| | | | | SSE | RMSE |
| Langmuir | $q_m$ (mg/g) | 14.24 | 0.9156 | 1.369 | 0.6756 |
| | $k_L$ (l/mg) | 0.8062 | | | |
| Freundlich | $k_F$ [(mg/g)(l/mg)$^{1/n}$] | 2.577 | 0.9841 | 0.2566 | 0.2924 |
| | $n$ (g/L) | 2.423 | | | |
| Temkin | $A$ | 42.72 | 0.8571 | 1.728 | 0.759 |
| | $B$ | 1.241 | | | |
| | $b$ (kJ/mol) | 2.029 | | | |

chitosan/PVA blend toward lead(II) ions. The separation factor is given by the expression as follows:

$$R_L = \frac{1}{1 + k_L C_0} \tag{10}$$

where $k_L$ = Langmuir constant and $C_0$ is the initial concentration of lead(II) ions. $R_L$ provides important information about the nature of adsorption. The nature of adsorption can be identified from the values of $R_L$ as follows: irreversible (if $R_L = 0$); favorable (if $0 < R_L < 1$); linear (if $R_L = 1$); and unfavurable (if $R_L > 1$). The experimental value of $R_L$ was found to be 0.1104–0.0242 for an initial lead(II) concentration of 10–50 mg/L, respectively, which lies in the range of 0–1, indicating that our system of adsorption is favorable.

The nonlinear for of Freundlich adsorption isothermal model [29] is as follows:

$$q_e = k_F C_e^{1/n} \tag{11}$$

where $k_F$ is Freundlich constant [(mg/g) (L/mg)$^{(1/n)}$] associated with the bonding energy and $n$ is a measure of deviation from adsorption linearity (g/L). The significance of $n$ value is that, it indicates the type of adsorption as follows: $n = 1$ indicates linearity of adsorption, $n < 1$ indicates the occurrence of chemisorption and $n > 1$ indicates the adsorption is physical adsorption. The experimental value of $n$ was found to be 2.423, which lies in between 0 and 10, indicating that the adsorption of lead(II) ions on chitosan/PVA blend was physisorption.

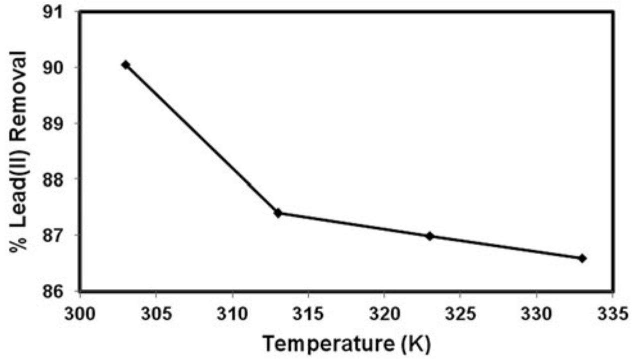

Fig. 12. Effect of temperature on the removal of lead(II) ions by chitosan/PVA.

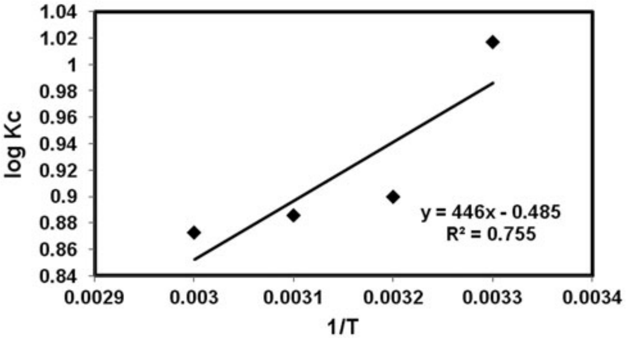

Fig. 13. Thermodynamic parameters involved in the removal of lead(II) ions by chitosan/PVA blend.

Table 6
Temperature vs. $K_c$ values at a concentration of 20 mg/L for the adsorption of lead(II) ions onto chitosan/PVA blend

| Temperature (℃) | $K_c$ |
|---|---|
| 30 | 10.05 |
| 40 | 7.936 |
| 50 | 7.692 |
| 60 | 7.463 |

The Temkin adsorption isotherm is as follows:

$$q_e = B \ln(A C_e) \tag{12}$$

$A$ is the equilibrium binding constant (L/mg) corresponds to maximum binding energy and the value of $A$ is 42.72 L/mg, $B$ is the constant relating the heat of adsorption $b_o$, $R$ is the universal gas constant ($R$ = 8.314 J/mol K), and $T$ is the temperature in $K$.

$$B = \frac{RT}{b_o} \tag{13}$$

Table 5
Thermodynamic parameters observed for the adsorption of lead(II) ions onto chitosan-blended PVA

| | | | ΔG° (kJ/mol) | | | |
|---|---|---|---|---|---|---|
| Initial concentration (mg/L) | ΔH° (kJ/mol) | ΔS° (J/mol/K) | 30℃ | 40℃ | 50℃ | 60℃ |
| 20 | −8.539 | −9.286 | −5.813 | −5.390 | −5.478 | −5.564 |

Table 7
Desorption of lead(II) ions from chitosan/PVA blend

| Initial lead(II) ion concentration (mg/L) | Removal efficiency (%) | % recovery of lead(II) ions 0.05 M HCl | 0.1 M HCl | 0.15 M HCl | 0.2 M HCl |
|---|---|---|---|---|---|
| 10 | 96.1 | 75.8 | 83.20 | 91.50 | 91.80 |
| 20 | 92.8 | 71.48 | 76.84 | 86.45 | 86.92 |
| 30 | 83.6 | 67.35 | 72.34 | 83.50 | 83.55 |
| 40 | 75.8 | 62.53 | 68.50 | 77.84 | 77.90 |
| 50 | 72.6 | 58.42 | 63.85 | 73.21 | 73.45 |

### 3.7. *Effect of temperature on the Pb(II) ion adsorption and thermodynamic studies*

Fig. 12 shows that the results of effect of temperature on the adsorption of lead(II) ions onto chitosan/PVA blend. The figure illustrates that the increase in temperature accounts for the decrease in percentage removal of lead(II) ions indicating the exothermic nature of adsorption. Maximum removal of lead(II) ions from the solution was observed at 30˚C.

The thermodynamic parameters such as standard Gibbs energy change ($\Delta G^\circ$), enthalpy change ($\Delta H^\circ$), and entropy change ($\Delta S^\circ$) of the adsorption of lead ions onto chitosan/PVA can be determined from the following equation:

$$\Delta G^\circ = -RT\ln\left(\frac{C_{\mathrm{Ae}}}{C_{\mathrm{e}}}\right) = -RT\ln(K_{\mathrm{c}}) \tag{14}$$

And

$$\log K_{\mathrm{c}} = \frac{\Delta S^\circ}{2.303RT} = \frac{\Delta H^\circ}{2.303RT} \tag{15}$$

where $K_{\mathrm{c}}$ = adsorption equilibrium constant, $C_{\mathrm{e}}$ is the equilibrium concentration of Pb(II)ions solution (mg/L), $C_{\mathrm{Ae}}$ is the amount of Pb(II) ions on chitosan/PVA/liter of solution at equilibrium (mg/L), $R$ is the universal gas constant (8.314 J/mol k) and $T$ is the temperature (K). The slope and intercept values were listed in Table 5, and the thermodynamic parameters were determined from Fig. 13. The figure illustrates a negative value of $\Delta G^\circ$ indicating the feasibility of adsorption process, negative value of $\Delta S^\circ$ indicates the enthalpy driven adsorption of lead ions onto chitosan/PVA, and negative value of $\Delta H^\circ$ indicates that the exothermal nature of adsorption system (Table 6).

### 3.8. *Desorption process*

Desorption process could be the right choice of regeneration and economical reuse/recycle of the used adsorbent, which opens up a wide door for the treatment of contaminated wastewater, reducing the aquatic pollution to a maximum level. Table 7 shows the removal efficiency as well percentage recovery of lead(II) ions for the concentration of lead(II) ions varying from 10 to 50 mg/L. It could be seen that the removal of lead(II) ions increases with an increase in the concentration of HCl and reaches a maximum constant value of 91.5% for 0.15 M.

## 4. Conclusion

This study focuses on the preparation of chitosan nanoparticles, when blended with PVA, acts as an effective adsorbent for the removal of lead(II) ions from its aqueous solution. The TEM image of the chitosan nanoparticles was observed to be 152.1 nm in size. The SEM morphological images of chitosan/PVA blend before and after adsorption of lead(II) ions have been effectively done. The varying physical parameters such as adsorbent dose, pH, initial ion concentration, contact time, and temperature were optimized to find the maximum % removal of lead(II) ions. Chitosan/PVA blend was found to be an effective adsorbent for lead(II) ions with 92.8% removal efficiency for a concentration of 20 mg/L of lead ion solution. Adsorption isotherms such as Langmuir, Freundlich, and Temkin models have been analyzed for the obtained equilibrium data, among which Freundlich isotherm best fits the experimental data. The maximum monolayer adsorption capacity was obtained to be 14.24 mg of lead(II) ions per g of chitosan/PVA blend. The kinetic data were checked for pseudo-first order, pseudo-second order, intraparticle diffusion and Boyd kinetic model and pseudo-second-order best fits the data, the calculated and the experimental values of $q_{\mathrm{e}}$ are in good correlation, hence which confirms the best suitability of pseudo-second-order kinetic model. The thermodynamic parameters were also deducted and infer that the adsorption process is exothermic in nature. And finally, the desorption of the lead(II) ions adsorbed on the chitosan/PVA blend had been successfully carried out, to recycle and reuse the adsorbent for further process of adsorption of heavy metal ions using the same adsorbent. Hence herewith to conclude from the above discussions, chitosan/PVA blends can be used as an efficient adsorbent for the removal of lead(II) ions containing wastewater.

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