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Adsorption of thallium (III) ion from aqueous solution using modified ZnO nanopowder

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ABSTRACT

In this study, the adsorption of thallium (III) ion from aqueous solutions onto modified ZnO nanopowder as a fairly low cost adsorbent has been investigated in batch mode. It was found that modification of the adsorbent was essential for obtaining the significant adsorption percentage. The adsorbent modified by sodium phosphate solution. The effect of experimental parameters such as initial pH of solution, contact time, adsorbent dosage, thallium initial concentration and temperature was studied. The results showed that the adsorption percentage was dependent on this parameters specially pH. The successful adsorption percentage of thallium (III) ion obtained at 25±1°C was 92.2-92.6%. The equilibrium data could be well described by the Freundlich isotherm but its fitting by Langmuir model was not so successful. Separation factor, R_L, values showed that modified ZnO nanopowder were favorable for the sorption of thallium (III) ion.

Keywords: Adsorption; Modified ZnO nanopowder; Thallium (III) ion; Langmuir isotherm; Freundlich isotherm

INTRODUCTION

There are various materials in waters and wastewaters that contaminate them. Among these pollutants, heavy metals such as lead, cadmium, mercury, copper, zinc and thallium are very toxic pollutants for environment but thallium toxicity is more than others for mammals [1, 2]. Thallium compounds enter the human body mainly through inhalation and food [3] and eating vegetables and fruits grown in contaminated soils to the thallium [4-6].

Thallium compounds can harm the bones, kidneys, liver, heart, lungs and nervous system and may be cause anorexia, headache, vomiting, diarrhea and even death [3, 6]. Therefore, removing the thallium compounds from waters and wastewaters is very necessary and has a specific importance.

Already, removing thallium from aqueous solutions has been performed by some adsorbents such as polyurethane foam [7], titania particle surfaces [8], silica gel [9], Aspergillus nigar biomass [10], dry biofilm biomass collected from a eutrophic lake [11], modified sugar beet pulp [12] and geological materials [13]. Also, some nano materials have been used to the thallium adsorption containing nano-Al_2O_3 [14],

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silver nanoparticles [15] and nano-TiO_2 [16]. In this paper, ZnO nanopowder was used, for the first time, as sorbent to remove thallium (III) ion from aqueous solutions. Among the nano materials, nano-ZnO is abundant and a fairly low cost sorbent. It was found that net charge of ZnO nanopowder in aqueous solution is positive, thus surface modification is necessary to obtain negatively charged ZnO nanopowder [17]. We performed the modification by sodium phosphate solution for adsorption of thallium (III).

EXPERIMENTAL

Apparatus

An AA220 Model Atomic Absorption Spectrometer (VARIAN Co., USA) was applied for measuring the concentration of Tl^{3+} and a 420A Model pH meter (ORION Co., USA) was used to evaluating pH of solutions. For separation of the adsorbent from the mixture, a model TDL80-2B centrifugal machine (Shanghai Anting Scientific Instrument Co., China) was used.

Materials

All chemicals used in this study were of analytical grade. Thallium (III) stock solution with appropriate concentration (250 ppm) was prepared by dissolving 0.1359 g of its nitrate ($Tl(NO_3)_3 . 3H_2O$, Fluka) in distilled water. ZnO nanopowder was prepared from TECNAN, Spain (Purity 99.983%, Average Particle Size (APS) 20-25 nm, Specific Surface Area (SSA) 5-50 m^2/g). Sodium phosphate ($Na_3PO_4.12H_2O$) was purchased from Merck, Germany.

Modification of adsorbent

In order to surface modification on nano-ZnO with negative charge for adsorbing position thallium ions, ZnO nanopowder (0.05 g) was suspended into 10 ml from 5% sodium phosphate solution and was shaken in a thermostatic orbit incubator shaker (Neolab, India) at 240 rpm for 60 min. Ultrasonic Bath (71020-DTH-E, Model 1510 DTH, 220 V, EMS Company) was used to prevent from aggregation of the nanopowder.

Adsorption experiments

The adsorption experiments were conducted in 100 mL flasks containing 50 mL of Tl (III) solution of known concentration (10 ppm) prepared from the dilution of 250 ppm stock solutions. The initial pH of each flask solution was adjusted to optimum value (pH 6) with 0.1 M HCl or 0.1 M NaOH solution. Then, the mixture of the modified nanopowder was added to each flask solution and the resultant mixture was shaken in a thermostatic orbit incubator shaker (Neolab, India) at 240 rpm for 60 min. Again, Ultrasonic Bath (71020-DTH-E, Model 1510 DTH, 220 V, EMS Company) was used to prevent from aggregation of the nanopowder. Upon completion, the sample of the mixture was removed from the flask and separated by centrifuging at 4000 rpm for 5 min. The obtained solution was later analyzed for residual Tl (III) ion. Then, the adsorption percentage (%adsorption) was determined as

$$\%Adsorption = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

Where C_i and C_f are the initial and the final concentration of Tl (III) in solution phase, respectively.

The amount of metal ion adsorbed per unit mass of adsorbent (q_e) was calculated using the following equation:

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

Where C_i and C_e represent initial and equilibrium concentrations (mg/L), respectively and V is the volume of the solution (L) and m is the mass of the adsorbent (g).

The average absolute value of relative error, AARE, was used to compare the predicted results with experimental data. This is defined as follows:

$$AARE\% = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|PredictedValue - ExperimentalValue\right|}{ExperimentalValue}\times 100 \qquad (3)$$

Which N is the number of data points.

Also, in this study the effect of various experimental parameters including concentration of modifier agent (sodium phosphate solution), initial pH of solution (5-7), contact time (15-60 min), amount of sorbent (0.05-0.18 g), thallium initial concentration (5-50 ppm) and temperature (25-60^{0}C) on the adsorption percentage of Tl(III) ion was investigated.

RESULTS AND DISCUSSION

Modification of the adsorbent by sodium phosphate solution

The adsorbent was modified with 1, 3, 5, 7, 10 and 15% w/v sodium phosphate solutions and adsorption process was carried out. The results showed that the modified adsorbent by 5% w/v sodium phosphate solution is the most suitable (Table 1, Fig. 1). Upon modification, PO_4^{3-} ions link to the adsorbent sites; this favors Tl^{3+} ion adsorption onto the surfaces of the adsorbent.

Table 1. Optimizing concentration of modifier agent (sodium phosphate solution)

Concentration of sodium phosphate (%w/v)	%Adsorption
1%	51.2
3%	74.6
5%	79.9
7%	75.7
10%	63.2
15%	54.9

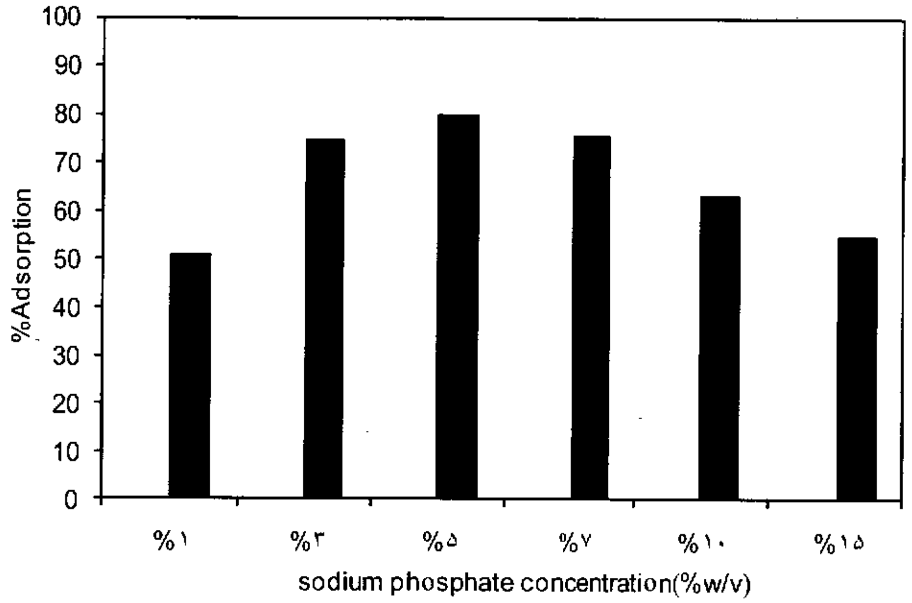

Fig. 1. Optimizing concentration of modifier agent (sodium phosphate).

The effect of initial pH of solution on adsorption percentage

Initial pH of the solutions was changed within the range of 5-7. At pH<5, ZnO nanopowder is dissolved in the solution and at pH>7, Tl (III) ion could be precipitate as $Tl(OH)_3$ ($K_{sp}=1.68 \times 10^{-44}$) [18]. The results are given in Table 2 and showed in Fig. 2. The optimum pH was obtained: pH=6.

The effect of contact time

The adsorption percentage of Tl (III) ion onto the modified ZnO nanopowder was affected the different contact times (see Table 3 and Fig. 3), while the other conditions maintained constant. The optimum contact time was 45 min. Decrease of adsorption percentages with contact time of 60 min may be due to desorption of thallium ions.

Table 2. Effect of initial pH of the solution on the adsorption percentage of Tl^{3+} ions (constant conditions: initial concentration of solution 10 mg/L, adsorbent dosage 0.05 g, contact time 60 min and temperature 25±1°C)

Initial pH of the solution	%Adsorption
5	68.9
6	79.4
7	78.8

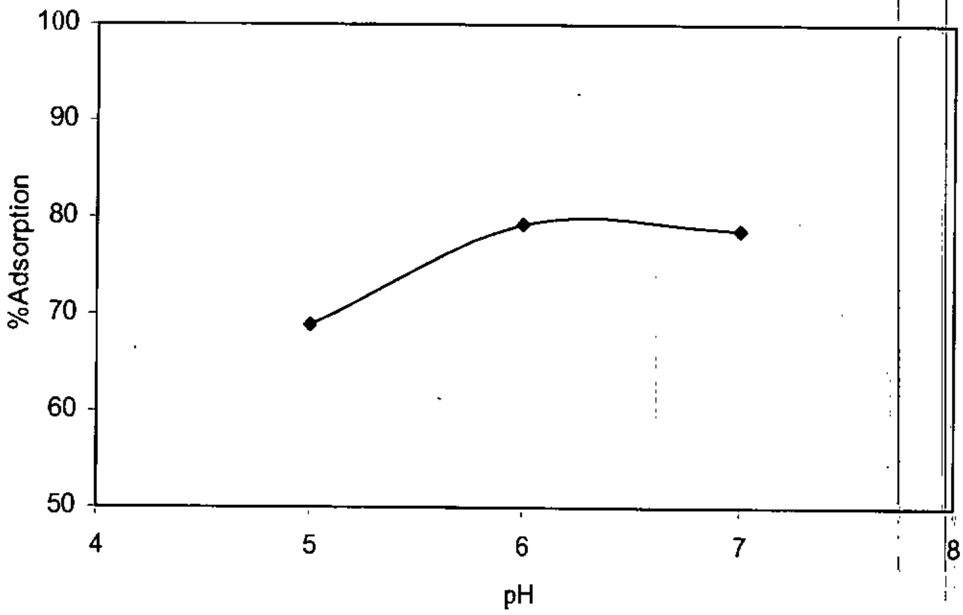

Fig. 2. The effect of initial pH of the solution on the adsorption percentage of Tl^{3+} ion, initial concentration, 10 mg/L; adsorbent dosage, 0.05 g; contact time, 60 min and temperature =25±1°C.

Table 3. The effect of contact time on the adsorption percentage (constant conditions: initial concentration of solution 10 mg/L, pH 6, adsorbent dosage 0.05 g and temperature 25±1^{0}C)

Contact Time (min)	%Adsorption
15	77.8
30	79.5
45	83.1
60	79.4

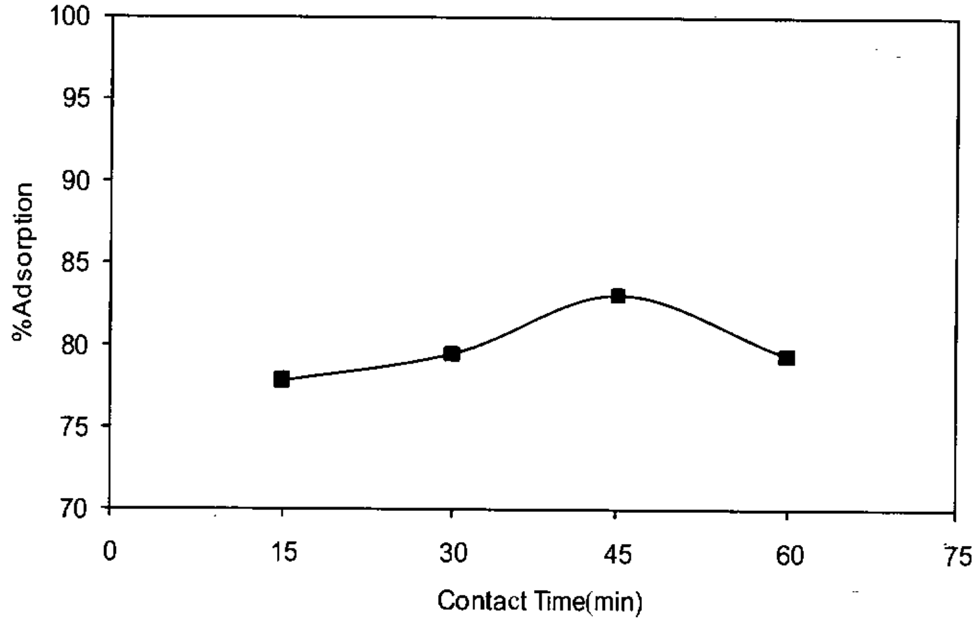

Fig. 3. The effect of contact time on the adsorption percentage, initial concentration, 10 mg/L; pH 6; adsorbent dosage, 0.05 g and temperature =25±1^{0}C.

The effect of sorbent dosage

The dosage of the sorbent in the test solutions was varied from 0.05 g to 0.18 g, where the other conditions were constant. The results are gathered in Table 4 and showed in Fig. 4. We observed that the dosage of 0.12 g was the most suitable.

The effect of temperature

The adsorption percentage was influenced upon temperature (Table 5, Fig. 5). The suitable temperature range was 25^{0}C. From the curve we can conclude that the adsorption may be exothermic.

Table 4. The effect of sorbent dosage on the adsorbent percentage of Tl(III) ion (constant conditions: initial concentration of solution 10 mg/L, pH 6, contact time 45 min and temperature 25±1°C)

Sorbent Dosage (g)	%Adsorption
0.03	73.3
0.05	83.1
0.07	84.8
0.1	87.5
0.12	88.7
0.15	88.4
0.18	87.6

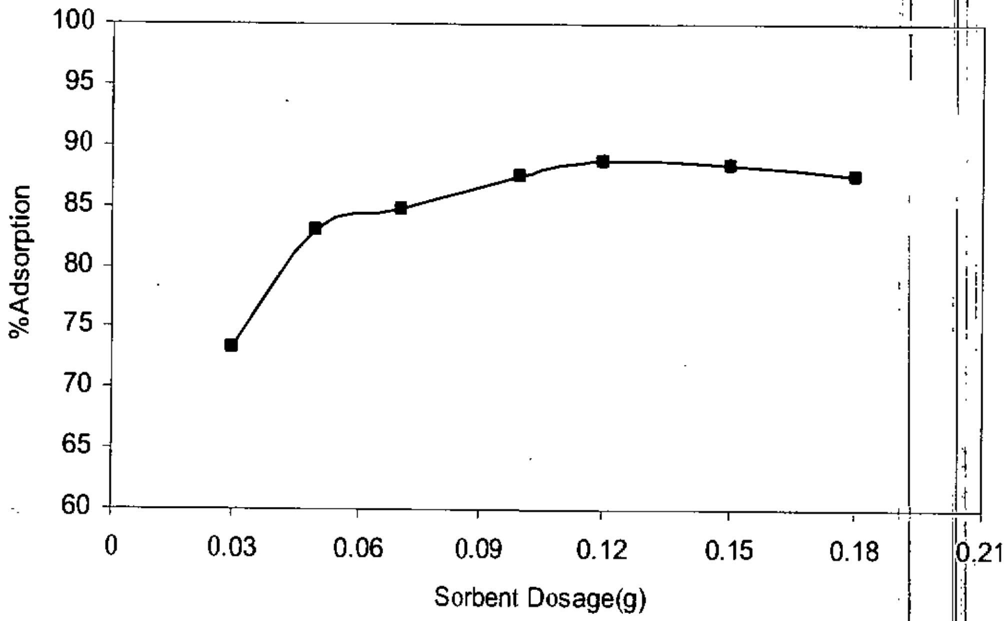

Fig. 4. The effect of sorbent dosage on the adsorbent percentage of Tl(III) ion, initial concentration, 10 mg/L; pH 6; contact time, 45 min and temperature =25±1°C.

The effect of temperature

The adsorption percentage was influenced upon temperature (Table 5, Fig. 5). The suitable temperature range was 25°C. From the curve we can conclude that the adsorption may be exothermic.

The effect of thallium initial concentration

Also, adsorption capacity affected by the thallium initial concentration. The adsorption percentage of Tl (III) ion onto modified ZnO nanopowder was measured in terms of initial concentrations of 5-50 ppm Tl^{3+} ion, where the other conditions were constant. The results are given in Table 6 and showed in Fig. 6. The suitable concentration range of Tl^{3+} ions was 30 mg/L.

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Table 5. The effect of temperature on adsorption percentage of Tl(III) ion (constant conditions: initial concentration of solution 10 mg/L, pH 6, contact time 45 min and adsorbent dosage 0.12 g)

Temperature (^{0}C)	%Adsorption
25	88.7
35	88.1
45	87.0
50	81.7
60	70.2

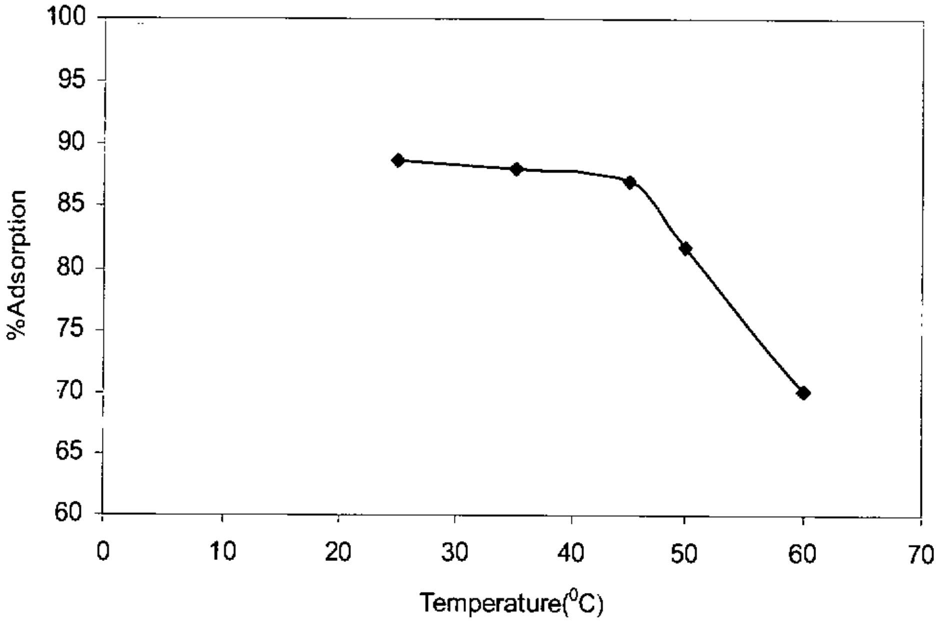

Fig. 5. The effect of temperature on the adsorption percentage of Tl(III) ion, initial concentration, 10 mg/L; pH 6; contact time, 45 min and adsorbent dosage, 0.12 g.

Table 6. The effect of initial concentration of thallium (III) on the adsorption percentage of Tl (III) (constant conditions: pH 6, contact time 45 min, adsorbent dosage 0.12 g and temperature 25±1°C)

Initial concentration of thallium (III) (mg/L)	Adsorption(%)
5	82.8
10	88.7
20	90.6
30	92.2
40	92.3
50	92.6

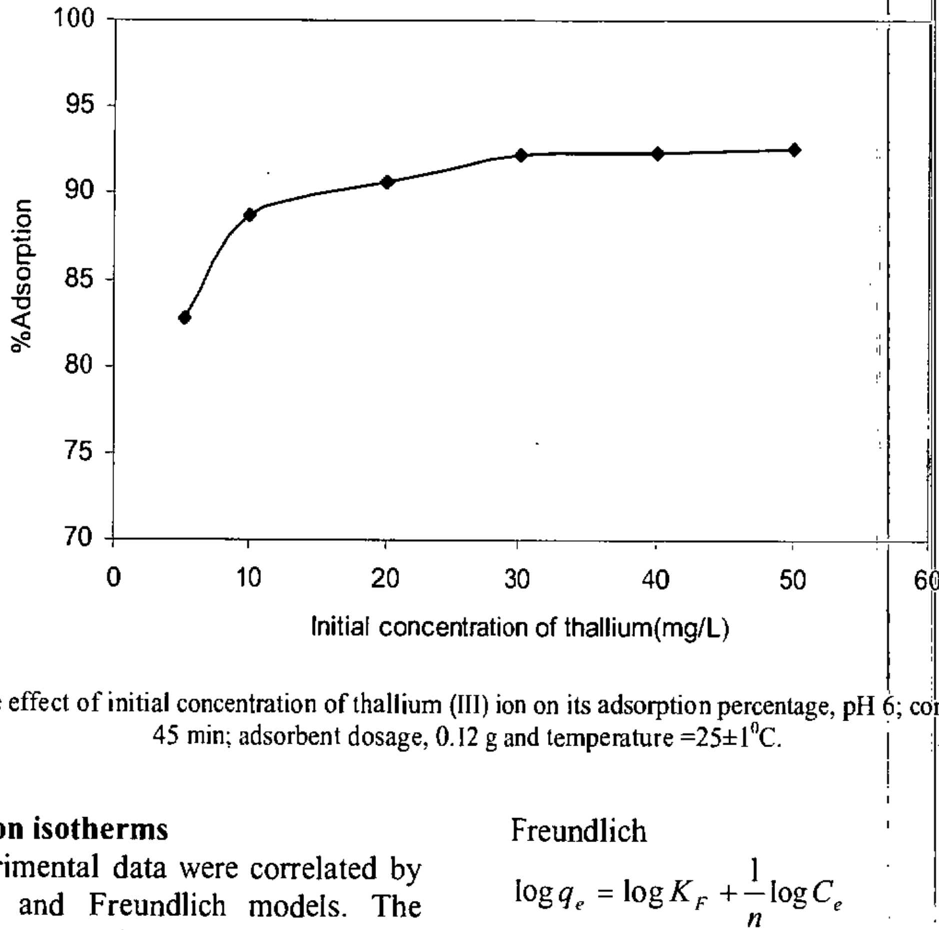

Fig. 6. The effect of initial concentration of thallium (III) ion on its adsorption percentage, pH 6; contact time, 45 min; adsorbent dosage, 0.12 g and temperature =25±1°C.

Adsorption isotherms

The experimental data were correlated by Langmuir and Freundlich models. The related linear equations are:

Langmuir equation:

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

Freundlich equation:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (5)$$

Where C_e (mg L^{-1}) and q_e (mg g^{-1}) are the liquid phase and solid phase concentrations of sorbate at equilibrium, respectively; K_L (L mg^{-1}), the Langmuir isotherm constant; q_m (mg g^{-1}), the maximum sorption capacity of Langmuir model; K_F, the Freundlich constant ($mg^{1-(1/n)}$ $L^{1/n}$ g^{-1}), and n is the heterogeneity factor.

At first, we correlated the adsorption data at different initial concentrations of Tl (III) ion in terms of the Langmuir isotherm (Eq. (4)). The curve of $1/q_e$ versus $1/C_e$ gives a straight line with a slope of $1/K_Lq_m$ and intercept of $1/q_m$ (Fig. 7a). Also, we examined the data according to the Freundlich isotherm (Eq. (5)). The plot of log q_e versus log C_e gives a straight line with slope 1/n and intercept log K_F (Fig 7b). It was observed that the experimental data have a very better agreement with the Freundlich isotherm than the Langmuir one because the values of regression coefficient and AARE % for the Freundlich isotherm are higher. Table 7c shows the parameters of the Langmuir and Freundlich models and theirs regression coefficients and AARE%. The results related to Langmuir and Freundlich isotherms were given in Tables 7a, b and shown in Fig. 7a, b respectively.

Table 7a. Sorption isotherms for thallium (III) ion onto the modified ZnO nanopowder: Langmuir isotherm (constant conditions: pH 6, contact time 45 min, adsorbent dosage 0.12 g and temperature 25±1°C)

C_i (mg/L)	C_e (mg/L)	q_e	$1/C_e$	$1/q_e$
5	0.86	1.73	1.16	0.58
10	1.13	3.70	0.89	0.27
20	1.89	7.55	0.53	0.13
30	2.33	11.53	0.43	0.09
40	3.08	15.38	0.33	0.07
50	3.68	19.30	0.27	0.05

Table 7b. Sorption isotherms for thallium (III) ion onto the modified ZnO nanopowder: Freundlich isotherm (constant conditions: pH 6, contact time 45 min, adsorbent dosage 0.12 g and temperature 25±1°C)

C_i (mg/L)	C_e (mg/L)	q_e	log C_e	log q_e
5	0.86	1.73	-0.07	0.24
10	1.13	3.70	0.05	0.57
20	1.89	7.55	0.28	0.88
30	2.33	11.53	0.37	1.06
40	3.08	15.38	0.49	1.19
50	3.68	19.30	0.57	1.29

Table 7c. Parameters of the Langmuir and Freundlich isotherm models

Langmuir isotherm model				Freundlich isotherm model			
K_L (L/mg)	q_m (mg/g)	R^2	AARE %	K_F ($mg^{1-(1/n)}$ $L^{1/n}$ g^{-1})	n	R^2	AARE %
0.246	7.3	0.9273	42.6	2.62	0.622	0.9812	17.3

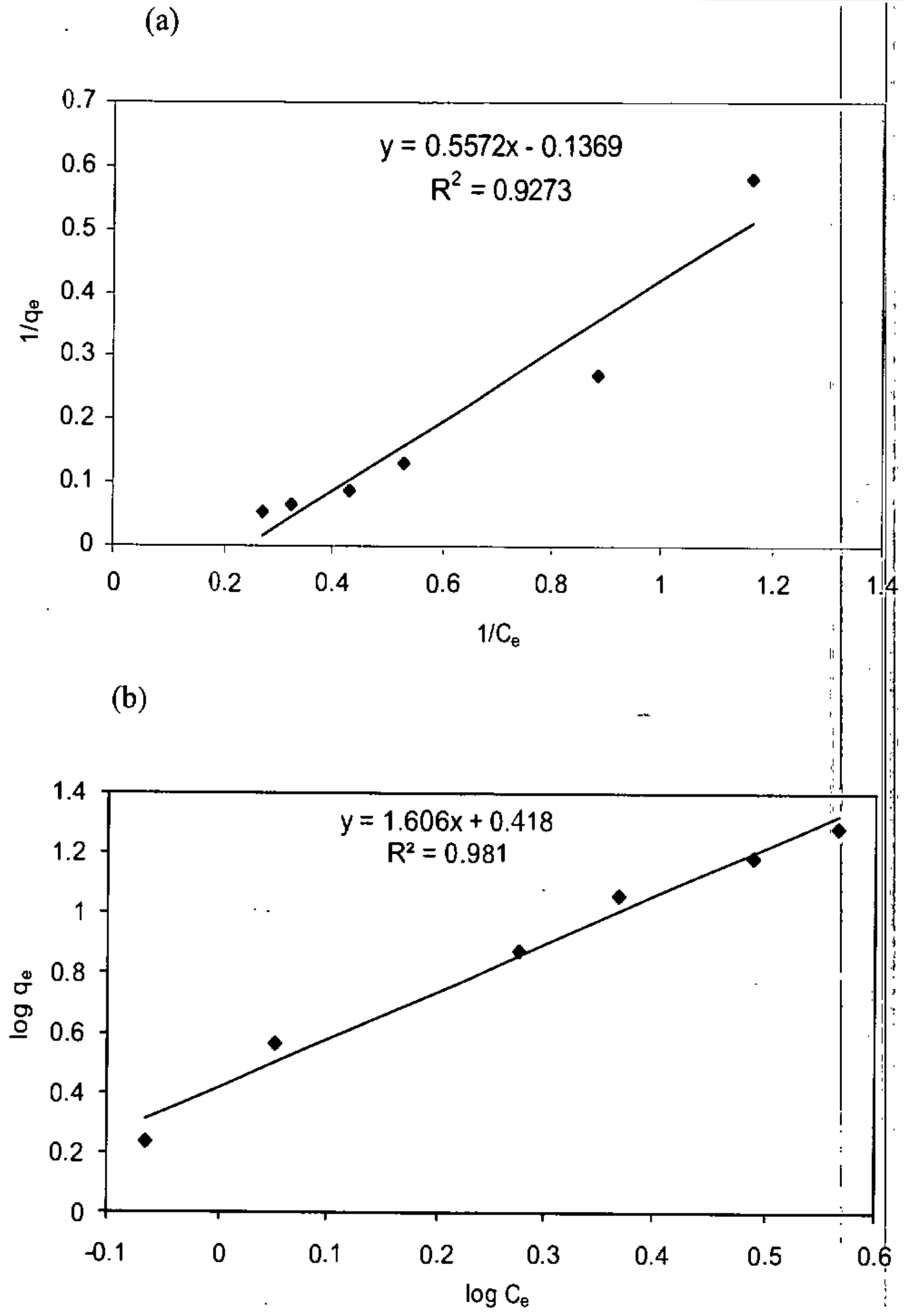

Fig. 7. Sorption isotherms for thallium (III) ion onto the modified ZnO nanopowder: (a) Langmuir isotherm and (b) Freundlich isotherm (conditions: pH 6; contact time, 45 min; adsorbent dosage, 0.12 g and temperature=25±1°C).

Constant separation factor, R_L, define the essential characteristics of the Langmuir isotherm by Eq. (6) [19].

$$R_L = \frac{1}{1+K_L C_i} \qquad (6)$$

Where K_L is the Langmuir constant and C_i is the initial concentration of the sorbate in solution.

This factor illustrates the shape of the isotherm and the nature of the adsorption process as below:

R_L value	**Nature of the process**
$R_L>1$	unfavorable
$R_L=1$	linear
$0<R_L<1$	favorable
$R_L=0$	irreversible

The calculated R_L values versus initial thallium (III) concentration were given in Table 8 and shown in Fig. 8. The value of R_L in the range of 0-1 at all initial thallium (III) concentrations confirms the favorable adsorption of Tl (III) ion.

Table 8. Separation factor for the adsorption of thallium (III) onto the modified ZnO nanopowder in terms of initial concentration of Tl^{3+}

C_i(mg/L)	R_L
5	0.45
10	0.29
20	0.17
30	0.12
40	0.09
50	0.08

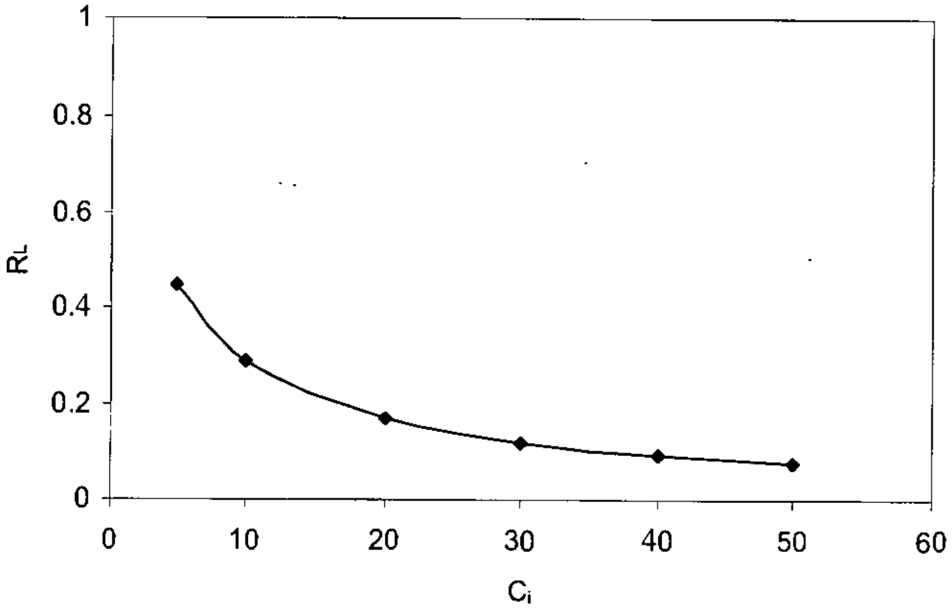

Fig. 8. Separation factor for the adsorption of thallium (III) onto the modified ZnO nanopowder in terms of initial concentration of Tl^{3+} ion.

CONCLUSION

This study showed that ZnO nanopowder can be modified with sodium phosphate solution and used as an adsorbent for the adsorption of Tl (III) ion from aqueous media. It was observed that 5% w/v sodium phosphate solution obtained the better adsorption percentage. Experimental data showed that the adsorption percentage was dependent on parameters such as initial pH of solution, contact time, adsorbent amount, temperature and thallium initial concentration. The optimum conditions were: pH 6; contact time, 45 min; adsorbent amount, 0.12 g; thallium initial concentration, 30-50 mg L^{-1} and temperature, 25^{0}C. Under the conditions, the successful adsorption percentage of thallium (III) ion on modified ZnO nanopowder obtained was 92.2-92.6%. The experimental data could be fairly good fitted by the Freundlich isotherm but its fitting by Langmuir model was not so successful. The R_L values illustrated that the modified ZnO nanopowder was favorable for the adsorption of thallium (III) ion.

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