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Kinetic Studies of the Adsorption of Thorium Ions onto Rice Husk from Aqueous Media: Linear and Nonlinear Approach

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ABSTRACT

The present works deals with the investigation of sorption kinetic of thorium ions onto rice husk employing batch method and radiotracer technique. The study was conducted in nitric acid media at ambient temperature. Maximum adsorption of 24.08 mg L^{-1} of thorium ion was observed at the optimized equilibrium time of 15 minutes, 0.1 g of adsorbent and nitric acid concentration of 1.0 × 10^{-4} mol L^{-1}. A comparison was made of the widely used pseudo first and second order kinetic models employing the method of least squares, for the adsorption of thorium ions onto rice husk. Different linear equations for first and second order kinetic were used for this purpose. The results showed the regression value "R^2" of 0.9711 for one linear equation of pseudo first order and 0.9997, 0.8877, 0.9315 and 0.9315, of type I, II, III, and IV models of linear equations for pseudo second order respectively. Kinetic parameters computed from linear and nonlinear forms of different models are reported and discussed. Among the linear expressions, Type I of the pseudo second order was found to be the most appropriate rate expression for the adsorption of thorium ions on rice husk.

1. Introduction

Thorium is long lived naturally occurring radio-nuclide and is widely distributed on the earth. Nuclear explosion tests, reprocessing of nuclear fuel, accidents in atomic power plants, its use as tracer studies and use of fertilizers are important factors of thorium induction into the environment [1]. Thorium accumulates mainly in lungs, liver, spleen and bone marrow, and eventually causes cancer of these organs [2]. Being long lived radioactive toxic metal the thorium ions must be removed from nuclear wastes before their disposal into water bodies. A number of techniques are being used for the removal of Th^{4+} ions form aqueous media such as, ion exchange resins [3], co-precipitation [4], solvent extraction [5] and adsorption. Adsorption is an effective method for the treatment of wastewaters containing radio nuclides. It has an edge over other techniques due to its simplicity, rapidness, low cost and high enrichment factor. The adsorbents used for thorium ions include metal oxides, perlite, activated carbon, bentonite, zeolites, PAN loaded polyurethane foam and biosorbents.

The kinetics study of batch adsorption process is one of the most important steps for designing of industrial processes [6]. The chemical kinetic explains how fast the rate of chemical reaction occurs. The nature of adsorption process depends on the physical or chemical characteristics of the adsorbents and on the system conditions. Different linear forms of the pseudo first order and pseudo second order kinetic equations are being used as the most fitted kinetic models for the adsorption process.

It was observed that during the transformation of non-linear forms of kinetic equations into some linear forms, the error distribution may alter from worse to better [7, 8] resulting in wide variations in the determination of kinetic parameters using different forms of model equations for a given adsorption process. Different kinetic parameters may be obtained by using different forms of model equations for a given data set of adsorption process.

The present study deals with a comparison of the non-linear and linear equations for pseudo first and pseudo-second-order kinetic models by determining the kinetic parameters and comparing them with the experimental data of the adsorption of thorium ions on rice husk, to assess the error structure in measuring the model parameters.

2. Experimental Procedure

2.1 Preparation of Radiotracer

The radiotracer of thorium (^{233}Th) was prepared by irradiating a known weight of specpure thorium nitrate from Johnson & Mathey, in a 10 MW swimming pool type reactor (PARR-1) of this institute for an appropriate time. The neutron flux used was 4.5×10^{13} cm^{-2} s^{-1}. After the required cooling time, the irradiated sample was dissolved in minimum amount of water and diluted to a suitable volume. The radionuclidic purity of the tracer was checked on 4K series of 85 Canberra Multichannel analyzer coupled with a 25 cm^3 Ge (Li) detector, where as a well type NaI scintillation counter (Canberra Inc.) coupled with a counter-

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scaler (Nuclear Chicago) was used for gross gamma counting.

2.2 Reagents

All the reagents used were of analytical grade. The husk of basmati rice used in this work was obtained from a rice mill which was thoroughly washed with distilled and deionized water to remove dust particles and was oven dried at 80^o C till constant weight. The dried husk was stored in a pre-cleaned air tight container and was used as such without any physical or chemical pre-treatment.

2.3 Sorption measurements

A known weight of rice husk (0.1 g) was taken in a 25 cm^3 screw caped culture tube and 4.0 cm^3 of standard acid solution was added into it. A fixed amount of stock radiotracer solution of thorium ions was pipetted into it. The contents were equilibrated on a mechanical wrist-action shaker (Vibromatic) for a specific time at a rate of 500 rpm. The contents of the tube were centrifuged for the separation of phases. The supernatant solution was withdrawn for activity measurement. The radioactivity of 1.0 cm^3 solutions was measured before (A_i) and after (A_f) equilibrium with a scintillation counter. All experiments were performed at ambient temperature (296 ± 1 K) unless otherwise specified.

The percentage adsorption of thorium ion from the solution was calculated using the following expression:

$$\% \text{ Adsorption} = \frac{A_i - A_f}{A_i} \times 100 \quad (1)$$

The extent of adsorption of thorium ions at time "t" was calculated as follows:

$$Q_t = \frac{C_o - C_t}{m_s} \quad (2)$$

where

A_i = initial radioactivity of thorium ions in solution (counts $min.^{-1}$).

A_f = final radioactivity of thorium ions in solution at equilibrium (counts $min.^{-1}$).

Q_t = amount of thorium ions adsorbed at time t (mg g^{-1}).

m_s = amount of adsorbent (g L^{-1}).

C_o = concentration of thorium ions at time t = 0 (mg L^{-1}).

C_t = concentration of metal at time t (mg L^{-1}).

3. Results and discussion

The adsorption of thorium ions from aqueous medium was investigated using rice husk as an adsorbent by optimizing nitric acid concentration employing batch method and radio tracer technique. The selection of parameters was made where maximum adsorption was observed. The reported results are the average of triplicate independent measurements with relative standard deviation of less than 3.5%.

3.1 Effect of variation in acid concentration

The adsorption of 12.04 mg L^{-1} of thorium ions was checked in nitric acid solutions. The concentration of acid was varied from 1.0 × 10^{-4} to 1.0 mol L^{-1}, using 0.1 g of rice husk and equilibration time of 20 minutes. The thorium ions concentration, equilibration time and the amount of rice husk were selected arbitrarily. The results are presented in Fig. 1, which revealed that maximum adsorption of thorium ions was observed at 1.0 × 10^{-4} mol L^{-1} of nitric acid solution. It was also observed that beyond this acid concentration, the percentage adsorption of thorium ions was decreased. The decrease in adsorption of thorium ions at higher acid concentration could be explained on the basis of the competition between positively charged thorium species and the excess of H^+ ions in the medium. The maximum adsorption of thorium ions on rice husk from 1.0 × 10^{-4} mol L^{-1} of nitric acid solution (pH = 4.0) is in accordance with the findings of Ishikawa et al., [9], where positively charged thorium ionic species [$Th(OH)^{3+}$, $Th(OH)_2^{2+}$, $Th_2(OH)_2^{6+}$ and $Th(OH)_3^+$] exist in aqueous solution. Since maximum adsorption of thorium ions on rice husk was observed at 1.0 × 10^{-4} mol L^{-1} of nitric acid solution, therefore, this concentration of nitric acid was used in all the subsequent experiments.

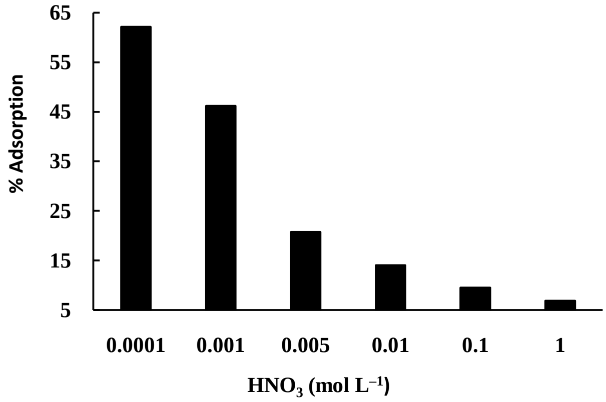

Fig. 1: Effect of nitric acid concentration on the adsorption of thorium ions on rice husk

3.2 Effect of equilibrium time

The effect of variation of time on the adsorption of Th^{+4} ions on 0.1 g of rice husk was studied using 4 cm^3 of 24.08 mg L^{-1} of thorium ion solution in 1.0 × 10^{-4} mol L^{-1} of nitric acid solution. The equilibration time was varied from 1 to 20 minutes and the results are represented in Fig. 2,

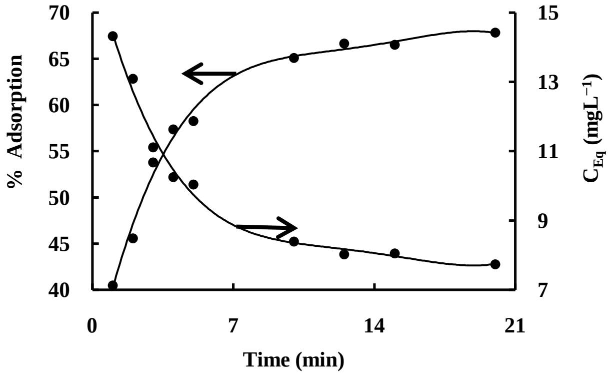

Fig. 2: Effect of time on the adsorption of thorium ions on rice husk

which shows that the percentage adsorption was increased with the increase in equilibration time. Maximum adsorption was observed at 15 minutes, beyond which there was no significant increase in the adsorption of thorium ions. Therefore, this equilibration time was considered to be sufficient for the adsorption of thorium ions on rice husk.

3.3 Kinetic models

The time dependent adsorption data of thorium ions on rice husk was subjected to different kinetic models. The experimental data of the thorium ions adsorption on rice husk was subjected to different nonlinear and linear forms of pseudo first order and pseudo second order models. Igor Pro 6.1.2, Wave Matrix software, was used for the calculation of kinetic parameters while using non-linear equations.

The Lagergren's pseudo first order kinetic equation [10] may be written as:

$$\frac{dQ_t}{dt} = k_1 (Q_e - Q_t) \quad (3)$$

The pseudo second order kinetic rate equation [11] can be expressed as :

$$\frac{dQ_t}{dt} = k_2 (Q_e - Q_t)^2 \quad (4)$$

where

Q_t = amount of thorium ions adsorbed at time "t" (mg g^{-1}).

Q_e = amount of thorium ions adsorbed at equilibrium (mg g^{-1}).

t = time in minutes.

k_1 = rate constant of the first order model (min^{-1}).

k_2 = rate constant of the second order model (g mg^{-1} min^{-1}).

After integration the equations (3) and (4), for the boundary conditions of $Q_t = 0$ at t = 0 and $Q_t = Q_t$ at t = t, followed by necessary rearrangements, the equations may be transformed to some nonlinear and linear forms of kinetic models, which are presented in Table 1. Among the listed equations in Table 1, there is one nonlinear and one linear equation for pseudo first order (PFO), whereas for pseudo second order (PSO), there is one nonlinear and four

Table 1: Non-linear and linear forms of pseudo first order and pseudo second order kinetic equations

Model	Equations	Plot	Parameters
Pseudo 1st order			
Nonlinear	$Q_t = Q_e(1 - e^{-kt})$	Q_t vs t	–
Linear form	$\log(Q_e - Q_t) = \log Q_e - (\frac{k_1}{2.303})\, t$	$\log(Q_e - Q_t)$ vs t	Slope = $k_1/2.303$ Intercept = $\log Q_e$
Pseudo 2nd order			
Non-linear	$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t}$	Q_t vs t	–
Linear Type I	$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$	t/Q_t vs t	Slope = $1/Q_e$ Intercept = $1/k_2 Q_e^2$
Linear Type II	$\frac{1}{Q_t} = \left(\frac{1}{k_2 Q_e^2}\right)\frac{1}{t} + \frac{t}{Q_e}$	$1/Q_t$ vs $1/t$	Slope = $1/k_2 Q_e^2$ Intercept = $1/Q_e$
Linear Type III	$Q_t = Q_e - \left(\frac{1}{k_2 Q_e}\right)\frac{Q_t}{t}$	Q_t vs Q_t/t	Slope = $1/k_2 Q_e$ Intercept = Q_e
Linear Type IV	$\frac{Q_t}{t} = k_2 Q_e^2 - k_2 Q_e Q_t$	Q_t/t vs Q_t	Slope = $k_2 Q_e$ Intercept = $k_2 Q_e^2$

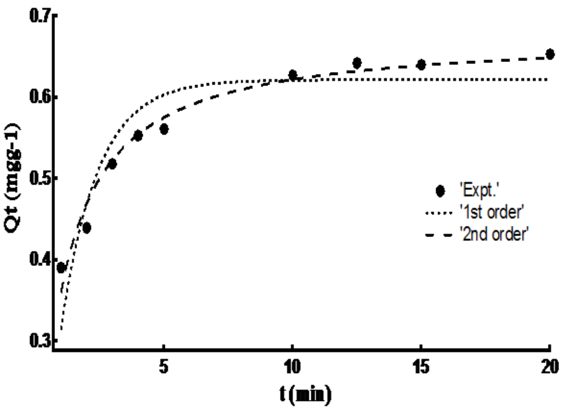

Fig. 3: Nonlinear plots of pseudo first order and pseudo second order kinetic models for the adsorption of thorium ions on rice husk

types of linear equations. The linear forms of PFO and PSO type I, equations are commonly used for kinetic studies of metal ions adsorption from aqueous media.

The non-linear forms of PFO and PSO kinetic models for the adsorption of thorium ions on rice husk are represented in Fig. 3 by plotting Q_t vs t, and the determined constants and theoretically calculated Q_e are given in Table 2. The linearized expression for PFO kinetic model has been shown in the form of a plot of $\log(Q_e\text{-}Q_t)$ vs t in Fig. 4 and the determined parameters from the slop and intercept are reported in Table 2. Likewise the PSO kinetic constant "k_2" and "Q_e" were obtained from the slopes and intercepts of the linear plots of t/Q_t vs t, $1/Q_t$ vs $1/t$, Q_t vs Q_t/t and Q_t/t vs Q_t for type I, II, III and IV pseudo second order expressions, respectively, and are shown in Fig. 5-6, whereas the determined parameters are listed in Table 2.

To compare the application of different models, the coefficient of determination "R^2" and Chi-square test "χ^2" were used as determining tools for the best-fit kinetic equations which may be calculated by the following expressions:

$$R^2 = \frac{\sum (q_{t,cal} - \bar{q}_{t,exp})^2}{\sum (q_{t,cal} - \bar{q}_{t,exp})^2 + \sum (q_{t,cal} - q_{t,exp})^2} \qquad (5)$$

and

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \qquad (6)$$

where

$q_{t,exp}$ = experimental adsorption at time t (mg g^{-1})

$q_{t,cal}$ = calculated adsorption at time t (mg g^{-1})

$\bar{q}_{t,exp}$ = average of $q_{t,exp.}$ (mg g^{-1})

q_e = equilibrium capacity from experimental data (mg g^{-1})

$q_{e,m}$ = calculated equilibrium capacity from the model (mg g^{-1}).

The computed values of "R^2" for linear equations and Chi-square "χ^2" values for nonlinear equations are shown in Table 2. The similarity of the data obtained from a non-linear model is usually established by comparison with the experimental data, χ^2 would be a smaller number & vice versa, whereas for linear models, maximum value of "R^2" is considered to be more favorable. The computed values of Chi-square test analysis "χ^2" for non-linear models of PFO and PSO were found to be 0.012 and 0.0022, respectively, which indicate that PSO model seems to be more plausible for the calculation of kinetic parameters for the adsorption of thorium ions on rice husk. Similarly the determined lower "R^2" value of 0.9711 (Table 2) revealed that the linear form of pseudo first order kinetic model is not an appropriate model to explain the sorption kinetic data of the thorium ions on rice husk.

The adsorption data of thorium ions on rice husk was subjected to one nonlinear and four linear models of the PSO as per parameters listed in Table 1, and the outcome is reproduced in Table 2. The perusal of the data presented in Table 2, suggested that PSO linear Type I form is the best fitted rate expression in terms of maximum "R^2" value of 0.9997, whereas for type II, III and IV, lower values of 0.8877, 0.9315 and 0.9315, respectively, were observed. The PSO type I equation is the most commonly used equation

Table 2: Determined parameters for non-linear and linear kinetic models for the adsorption of Th^{+4} ions on rice husk

Model	Rate constant, k (g mg^{-1} min^{-1})	Q_e (mg g^{-1})	% Error	χ^2	R^2
PFO Non-linear	0.702	0.621	4.900	0.012	–
PFO Linear	0.380	0.521	20.214	–	0.9711
PSO Non-linear	1.668	0.676	−3.522	0.0022	–
PSO Linear Type I	1.448	0.691	−5.819	–	0.9997
PSO Linear Type II	1.410	1.558	−138.59	–	0.8877
PSO Linear Type III	1.882	0.666	−1.990	–	0.9315
PSO Linear Type IV	1.732	0.674	−3.216	–	0.9315
Experimental Q_e = 0.653 (mg g^{-1})					

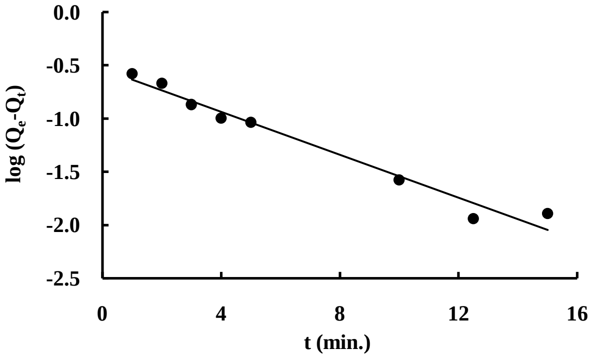

Fig. 4: Linear plot of pseudo first order kinetic model for the adsorption of thorium ions on rice husk

by various researchers for different sorption systems [12, 13]. The calculated values of rate constant from the four linear types of pseudo second order (Table 2) were close to each other.

The variation in the determined values by different linearized models using the same experimental data could be ascribed to the extent of complexities and problems associated during the linearization process of a non-linear form. Keeping in view of these facts, it will be more appropriate to apply non-linear expression to determine the kinetic parameters since the error distribution do not alter during its execution. However for the application of nonlinear model one has to optimize certain equation parameters to minimize Chi-square value as much as possible.

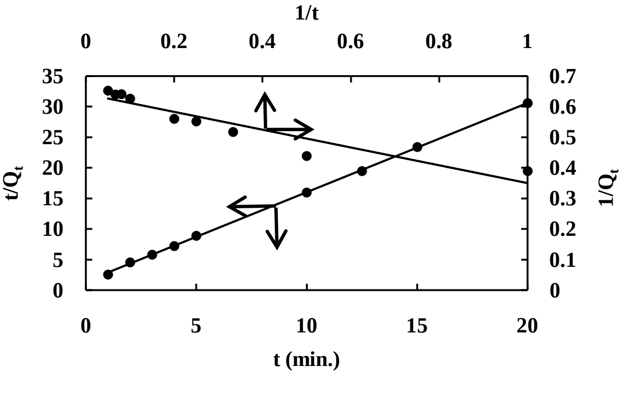

Fig. 5: Linear plots of pseudo second order type I and II kinetic models for the adsorption of thorium ions on rice husk

By the comparison of the Q_e values for pseudo first-order kinetic obtained by non-linear equation (0.621mg g^{-1}) and linear equation (0.521mgg^{-1}), it was observed that results obtained by linear model was 20.21 % higher as compared to the experimentally determined value of 0.653 mg g^{-1} indicating the non applicability of the linear model to the adsorption data of the thorium ions on rice husk. However the results obtained by the nonlinear model were closer to the experimental value and should be a better option for its applicability.

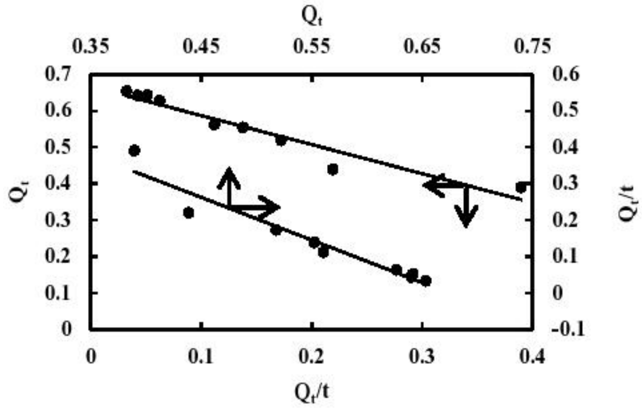

Fig. 6: Linear plots of pseudo second order type III and IV kinetic models for the adsorption of thorium ions on rice husk

The "Q_e" value obtained by nonlinear PSO model (0.676 mg g^{-1}) was quite closer to that of the experimentally determined value. Similar observations have been reported for the adsorption of methylene blue on activated carbon [6]. The application of linear equations of PSO models the type II produce significantly different results (1.558 mg g^{-1}) as compared to experimental value with an error of 139 % (Table 2). However the results obtained from rest of the three linear models i.e., type I, III and IV, were almost similar to the experimentally determined value with minimum deviation of 1.99 % from Type III. Although the determined "Q_e" value by PSO Type III is closer to experimental value but has lower value (0.9315) of coefficient of determination. Therefore, on the basis of minimum difference between the theoretically and experimentally determined "Q_e" values and maximum observed value of "R^2", it is concluded that the PSO, Type I equation should be a better option for the evaluation of kinetic parameters for the adsorption of thorium ions on rice husk while using linear equations.

4. Conclusions

Rice husk proved to be a good adsorbent for the removal of thorium ions from 1.0×10^{-4} mol L^{-1} solution of nitric acid. The sorption of thorium ions on rice husk was found to be better explained by the pseudo second order kinetic model. The study revealed that the non-linear forms of pseudo first order and pseudo second order kinetics models were superior to the linear forms. Among the four tested linear forms of pseudo second order, the Type I seems to be a better option for the calculation of kinetic parameters for the adsorption of thorium ions on rice husk.

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