

Assessment of kinetic models on Fe adsorption in groundwater using high-quality limestone

N A Akbar^{1,3}, N A F Mohd Kamil⁴, N S Md Zin⁴, M N Adlan^{1,3} and H A Aziz^{1,2}

¹School of Civil Engineering, University Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

²Solid Waste Management Cluster, Engineering Campus, Universiti Sains Malaysia

³Faculty of Civil Engineering, UiTM Pulau Pinang, 13500 Permatang Pauh, Penang, Malaysia

⁴Water and Environmental Engineering Department, Faculty of Civil & Environmental Engineering Universiti Tun Hussein Onn Malaysia, Batu Pahat, Johor, Malaysia

E-mail: cehamidi@usm.my

Abstract. During the groundwater pumping process, dissolved Fe²⁺ is oxidized into Fe³⁺ and produce rust-coloured iron mineral. Adsorption kinetic models are used to evaluate the performance of limestone adsorbent and describe the mechanism of adsorption and the diffusion processes of Fe adsorption in groundwater. This work presents the best kinetic model of Fe adsorption, which was chosen based on a higher value of coefficient correlation, R². A batch adsorption experiment was conducted for various contact times ranging from 0 to 135 minutes. From the results of the batch study, three kinetic models were analyzed for Fe removal onto limestone sorbent, including the pseudo-first order (PFO), pseudo-second order (PSO) and intra-particle diffusion (IPD) models. Results show that the adsorption kinetic models follow the sequence: PSO > PFO > IPD, where the values of R² are 0.997 > 0.919 > 0.918. A high value of R² (0.997) reveals better fitted experimental data. Furthermore, the value of q_{e cal} in the PSO kinetic model is very near to q_{e exp} rather than that in other models. This finding therefore suggests that the PSO kinetic model has the good fitted with the experimental data which involved chemisorption process of divalent Fe removal in groundwater solution. Thus, limestone adsorbent media found to be an alternative and effective treatment of Fe removal from groundwater.

1. Introduction

Limestone consists of dissolved calcium ions and carbon dioxide that associate to form a calcium carbonate material. This material deposited and changed into sedimentary rock. Most studies from the literature found that limestone has the potential to remove more than nine-tenths of heavy metals, from water and wastewater [1-4]. Low-grade limestone can remove only 75% of heavy metals; by contrast, high-grade limestone can remove more than 90% of heavy metals [5]. In this study, a high-quality limestone was used for batch adsorption study. The high-quality limestone media contained a majority of CaCO₃ of 97.9% based on the elemental analysis. On the contrary, this adsorbent media also contained a variety of impurities including 0.87% MgO, 0.86% SiO₂, Al₂O₃ and others [6]. To obtain effective removal of Fe, it is important to use limestone with high concentration of CO₃. Previous studies found that high-quality limestone can remove more than 90% of Fe through batch adsorption process



for groundwater samples [7]. In the study, the removal of Fe is followed by the monolayer Langmuir adsorption isotherm. In the Langmuir isotherm, the force of attraction between a divalent Fe ion and limestone sorbent consists of chemical bond force [8]. The adsorption isotherm has been discussed only in terms of the interaction between the adsorbate and adsorbent. However, no study on the kinetics of Fe removal onto limestone media has been done to understand the dynamics of adsorption in relation to time. Hence, this gap of knowledge on the mechanism of the adsorption and diffusion processes of Fe needs to be explored as a new alternative for the treatments of groundwater contaminated with heavy metals.

Currently, many types of kinetic models are applied to describe the mechanism of adsorption, such as the pseudo-first order [9], pseudo-second order [10-11], Elovich [10], particle diffusion [12], and intra-particle diffusion model [13]. According to the previous literature, most of the metal adsorption behavior follows the pseudo-second order kinetic model [14-19]. However, the result on the adsorption of organic pollutants onto non-polar polymeric adsorbents not fitted to the previous model [20]. Thus, in the present study, three different types of kinetic models are analyzed and discussed. This study presents the best kinetic model of the Fe adsorption process, which is chosen based on a higher value of the coefficient correlation, R^2 . The objective of this paper is to evaluate the different types of kinetic models for Fe removal onto limestone for groundwater treatment.

2. Material and Method

This section consists of characteristic of adsorbent properties, site sampling, experimental works and analysis of adsorption kinetic models.

2.1. Limestone characteristic

In this study, the limestone adsorbent media was bought from the marble factory located in Ipoh Perak. The adsorbent was pulverized into fine powder form until the particle size could pass through the size of 0.75 μm for elemental and chemical analysis using X-Ray fluorescent (Rigaku RIX 3000). For particle size distribution analysis, about 1 kg of the adsorbent media was passed through the sieves using a mechanical sieve shaker. During the batch adsorption experiment, the limestone was rinsed using ultra-pure water (UPW) to remove dirt and dust. Then, the adsorbent media was dried overnight at 105^o C using air circulation oven.

2.2. Groundwater sampling

In this study, a source of groundwater was collected from USM borehole which located at GPS coordinate of 5° 08' 50.5" N, 100° 29' 34.7". A groundwater sample was taken from the USM borehole located near the School of Civil Engineering, USM Engineering Campus, Nibong Tebal Penang, at the coordinates of 5° 08' 50.5" N, 100° 29' 34.7" E. The characteristics of the groundwater samples were monitored for six months. During the pumping process of groundwater, the sample was pumped out and purified for 30 minutes to grid out its impurities. After 30 minutes of pumping process, the sample was collected using polyethylene bottle. Then, the sample was preserved at 4°C and transported into the USM Environmental Laboratory for characteristic analysis. Analysis of Fe concentration was conducted using Atomic Absorption Spectrometer (AAS) (model: AAnalyst 800 – Perkin Elmer).

2.3. Batch study adsorption

A batch study experiment was conducted using various contact times ranging from 0 to 135 minutes. A total of 40 g of the limestone medium was added in 200 mL of groundwater solution in each conical flask. The sample was mounted on a shaker and was shaken for optimum shaking time of 350 rpm [26]. After 90 minutes of settling process, about 10 to 20 mL of the supernatant sample was extracted for Fe analysis using an AAS instrument. From the results of the batch experiment, analysis on the equilibrium kinetic models were carried out for adsorption process.

2.4. Adsorption kinetic models

Three mathematical models were presented to describe the kinetics of Fe in this study. The models were the PFO, PSO and IPD models.

2.4.1 PFO Model. The PFO kinetic model is called Lagergen's first order rate equation, and the linear equation is shown in equation (1).

$$\log(q_e - q_t) = \log q_e - \frac{tk_1}{2.303} \quad (1)$$

where q_e and q_t are the equilibrium at any time (t) capacity of metal adsorbed (mg/g) and k_1 is the constant rate of adsorption. k_1 was determined from the gradient of $\log(q_e - q_t)$ versus t graph.

2.4.2 PSO Kinetic Model. The PSO kinetic model is commonly used to depict the kinetic process of divalent metals ions onto adsorbent media [20]. The equation of the model is shown by the following expression:

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

where k_2 is the PSO rate constant adsorption ($\text{g mg}^{-1} \text{min}^{-1}$). The constant can be calculated from the intercept of t/q_t versus t graph, and the equilibrium from the gradient of the graph [20].

2.4.3 IPD Model. The analysis of the diffusion model can be described using the intra-particle model. This kinetic model was proposed by Weber and Torris [24]. The linearize equation is expressed as in equation (3).

$$q_t = k_{di} t^{1/2} + c \quad (3)$$

where k_{di} ($\text{mg g}^{-1} \text{min}^{-1/2}$) represents the IPD rate constant and c (mg/g) is the intercept to the adsorption stage. k_{di} can be calculated from the slope of plot q_t versus $t^{1/2}$.

3. Result and Discussion

3.1. Limestone characteristic

The mineralogy analysis of limestone adsorbent media was carried out using XRF analysis. Based on the XRF analysis results, limestone predominant to 97.9% of CaCO_3 and less of impurities including 0.87% MgO, 0.86% SiO_2 , Al_2O_3 and other elements which increased the sorption capacity. The results indicate that high quality of limestone (>90% of CaCO_3) sample used in this study. The effectiveness of Fe adsorption was proportional to the concentration of CO_3 in the limestone media. Furthermore, an adsorbent with particle size in a range of 1.18 mm – 2 mm was selected as adsorbent media based on a particle size analysis experiment.

3.2. Characteristics of groundwater sampling

The study on the characteristics of groundwater samples obtained from borehole in USM was conducted within 6 months period. During this period, the samples was taken for 12 times. According to AAS analysis, the average of Fe concentration in the USM borehole was 1.48 mg/L which exceeded the acceptable limit of raw (Fe < 1 mg/L) and drinking water (Fe < 0.3 mg/L) standards. The high-quality limestone was proposed as an alternative of treatment method for contaminated groundwater.

3.3. Kinetic study

Analysis on the kinetic model was employed to investigate the adsorption rate and uptake mechanism of Fe adsorption and limestone adsorbent. In the present experimental data, the suitability of three kinetic models was measured using R^2 values and comparison between experimental and calculate value of adsorption capacity. From the results shown in table 1, the models followed this sequence: PSO > PFO > IPD.

3.3.1. PFO Kinetic model. The scatter plot of $\log(q_e - q_t)$ versus time shows the result of the correlation coefficient of Fe removal in the PFO kinetic model. The R^2 value is 0.9186, and the value of $q_{e \text{ cal}}$ (0.0275 mg g^{-1}) is not very close to $q_{e \text{ exp}}$ (0.01709 mg g^{-1}). According to the analysis result as shown in table 1, adsorption process of Fe was not followed PFO kinetic model.

3.3.2. PSO Kinetic Model. The PSO kinetic model was used to describe the chemical adsorption and strong bonding between the limestone sorbent and divalent Fe ion. The PSO kinetic give highest value of correlation coefficient ($r^2 > 0.99$) compared to the both PFO and IPD models, as shown in figure 1. The value of $q_{e \text{ cal}}$ (0.0189 mg/g) in the PSO model was very near to the $q_{e \text{ exp}}$ (0.017 mg/g) rather than that in the other model. The value of the PSO rate constant, k_2 , was 5.913 $\text{g.mg}^{-1} \text{min}^{-1}$. This means that the Fe uptake from the limestone adsorbent from the groundwater solution was rapid [25]. From the result, chemisorption is the rate of the determining step, which involves ion exchange reaction between the limestone sorbent and Fe in divalent form [20].

3.3.3 IPD model. Three different regions represent the adsorption process of Fe from the analysis results as shown in table 2. The first region represents the stage of film diffusion, the second region represents the intra-particle diffusion, and the final region represents the equilibrium or saturation. The value of R^2 is 0.918 for the overall adsorption process. In the multi-linearity adsorption process, the constant and correlation values are shown in table 2. The values of R^2 in the first region ($R^2 = 0.998$) are greater than in the second region ($R^2 > 0.982$). In the first region, the adsorption is completed within 30 minutes, when the initial concentration of Fe in the initial stage of adsorption is high. The movement of particles occurs through random kinetic movement. A high metal concentration provides better driving force to the external mass transfer process. In the second region, the sorption period is between 30 to 75 minutes. The values of k_{d1} (0.0025) are greater than those of k_{d2} (0.0011), which indicates that intra-particle diffusion is a gradual adsorption process. The concentration of the remaining Fe in the groundwater solution decreases when $k_{d1} > k_{d2} > k_{d3}$ [14]. The value of the interception, C presented the boundary layer effect. A smaller value of the intercept indicates that the external mass transfer of heavy metals is not significant in the adsorption process

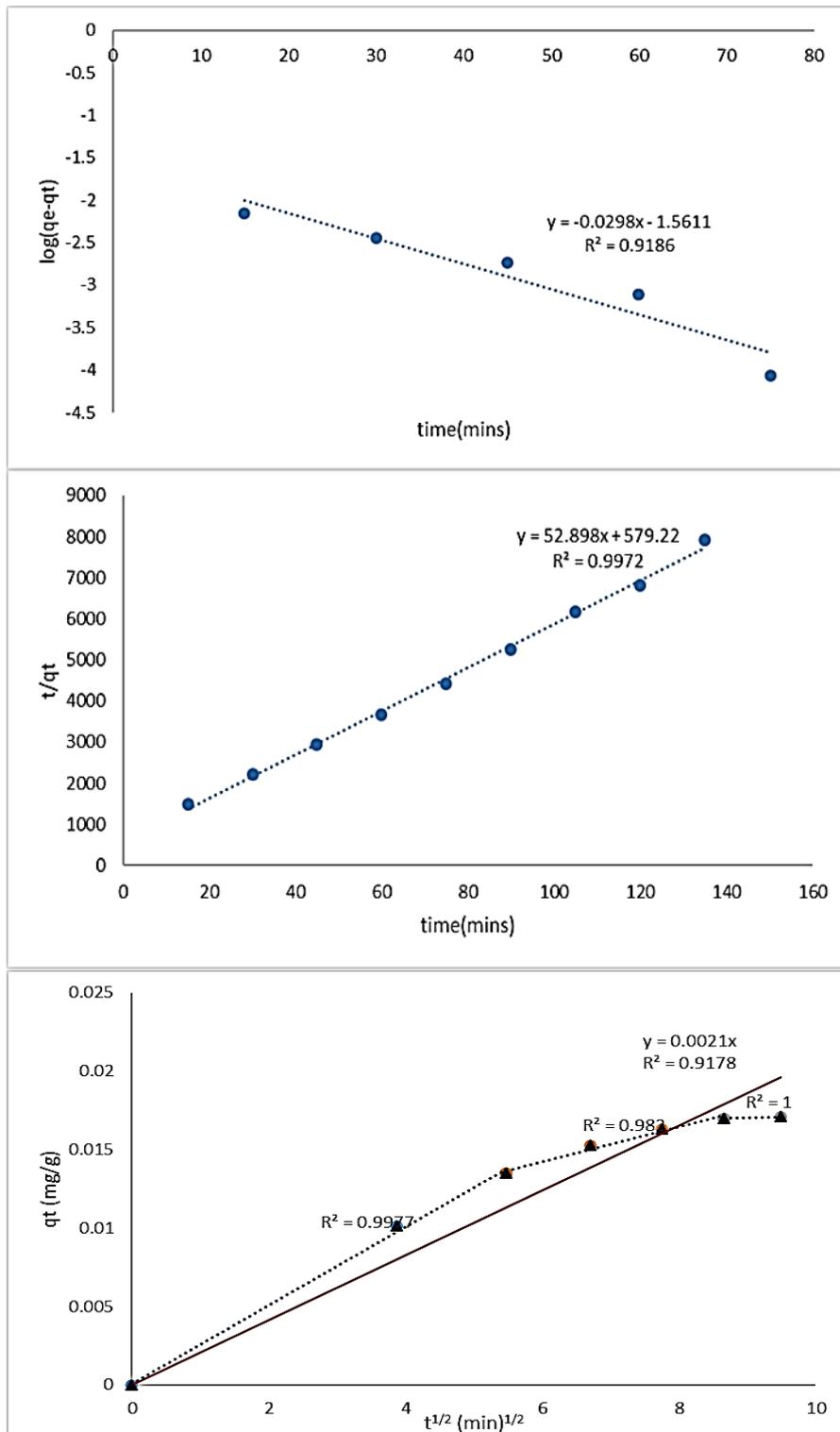


Figure 1. Kinetic models of Fe adsorption; a) PFO, b) PSO and c) IPD

Table 1. Summary results of the constant parameters and correlation coefficient of the adsorption kinetics model.

Kinetic model	Constant parameters	Result
PFO	q_{exp} (mg g ⁻¹)	0.017
	r^2	0.919
	k_1 (min ⁻¹)	0.069
	$q_{e cal}$ (mg/g)	0.0275
PSO	r^2	0.997
	k_2 (g mg ⁻¹ min ⁻¹)	5.913
	$q_{e cal}$ (mg/g)	0.0189
IPD	r^2	0.918
	k_d (mg.g ⁻¹ min ⁻¹)	0.0021
	$q_{e cal}$ (mg/g)	0.0199

Table 2. Summary of the constants and correlation coefficients for IPD models

Metal	IPD model								
	k_{d1}	k_{d2}	k_{d3}	C_1	C_2	C_3	R_1^2	R_2^2	R_3^2
Fe	0.0025	0.0011	0.0001	0.0001	0.0076	0.0161	0.998	0.982	1

4. Conclusion

Three kinetic models, the PFO, PSO and IPD models are employed to describe the mechanism of adsorption process. the PSO kinetic model is the best adsorption kinetic model than both PFO and IPD models. In this model, the values of the correlation coefficient, R^2 , for Fe adsorption onto limestone are much closer to 1. The highest value of R^2 (> 0.99) of Fe adsorption verifies the kinetic model. Furthermore, the value of $q_{e cal}$ in the PSO model is most approaching to $q_{e exp}$ compared to other models. These findings suggest that the PSO kinetic model has the good fitting with the experimental data, where chemisorption processes are involved in divalent Fe adsorption onto limestone sorbent from groundwater samples [24].

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References

- [1] Aziz H A, Adlan M N, Ariffin K S 2008 Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) removal from water in Malaysia: post treatment by high quality limestone. *Bioresource technology* **99**(6) 1578
- [2] Aziz H A, Smith PG 1992 The influence of pH and coarse media on manganese precipitation from water *Water Research* **26**(6): 853
- [3] Aziz H A, Yusoff M S, Adlan M N, Adnan N H, Alias S 2004 Physico-chemical removal of iron from semi-aerobic landfill leachate by limestone filter. *Waste management (New York, N.Y.)* **24**(4): pp 353–358
- [4] Aziz H A, Othman N, Yusuff M S, Basri D R, Ashaari F A, Adlan M N, Perwira M 2001 Removal of copper from water using limestone filtration technique. Determination of mechanism of removal. *Environment international* **26**(5-6) 395
- [5] Sdiri A, Higashi T, Jamoussi F, Bouaziz S 2012 Effects of impurities on the removal of heavy metal by natural limestone in aqueous system *Journal of Environmental Management* **93**(1): 45

- [6] Akbar N A, Aziz H A, Adlan M N 2015a Potential use of ozonation with limestone adsorption in groundwater. *Jurnal Teknologi (Science & Engineering)* **58** 85
- [7] Akbar N A, Aziz H A, Adlan M N 2015b Iron and manganese removal from groundwater using high quality limestone *Applied Mechanics and Materials* **802** 460
- [8] Jusoh A, Cheng W H, Low W M, Nora'aini A, Megat Mohd Noor M J 2005 Study on the removal of iron and manganese in groundwater by granular activated carbon *Desalination* **182**(1-3) 347
- [9] Ho Y S 2004 Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics* **59**(1) 171
- [10] Ho Y S, Mc Kay G 1998 A comparison of chemisorption kinetic models applied to pollutant removal on various sorbent *Trans IChemE* **76** 333
- [11] Wu F, Tseng R, Huang S, Juang R 2009 Characteristic of pseudo-second-order kinetic model for liquid-phase adsorption : A mini review *Chemical Engineering Journal* **151** 1
- [12] Liu X, Zhang L 2015 Removal of phosphat anions using modified chitosan beads : Adsorption kinetic, isotherm and mechanism studies *Powder Technology* **277** 112
- [13] Singh S K, Townsend T G, Mazyck D, Boyer T H 2012 Equilibrium and intra-particle diffusion of stabilized landfill leachate onto micro and meso porous activated carbon *Water Research* **46** 491
- [14] Ma X, Li L, Yang L, Su C, Wang K, Yuan S, Zhou J 2012 Adsorption of heavy metal ions using hierarchical CaCO₃ – maltose meso/macroporous hybrid materials: Adsorption isotherms and kinetic studies *Journal of Hazardous Materials* **209-210**: 467
- [15] Glocheux Y, Pasarin M M, Albadarin A B, Allen S J, Walker G M 2013 Removal of arsenic from groundwater by adsorption onto an acidified laterite by-product *Chemical Engineering Journal* **228** 565
- [16] Vitela-Rodriguez A V, Rangel-Mendez J R 2013 Arsenic removal by modified activated carbons with iron hydro (oxide) nanoparticles *Journal of environmental management* **114** 225
- [17] Kumar P S, Kirthika K 2009 Equilibrium and kinetic study of adsorption of nickle from aqueous solution onto bael tree leaf powder *Journal of Engineering Science and Technology* **4** (4) 351
- [18] Adeoye M D, Azeez L A, Lawal A A T, Olayiwola O A , Shitta O R 2014 Kinetic and equilibrium studies of heavy metal remediation potential of Helix pomentia *African Journal of Pure and Applied Chemistry* **8**(9) 123
- [19] Ahmad S Z N, Hamdan R, Mohamed W A W, Othman N, Zin N S M and Musa S 2017 Comparisons Study of Phosphate Removal in Unaerated and Aerated High Calcium Steel Slag Filter System of Different pH Feed *MATEC Web of Conferences* **103** 06018
- [20] Qiu H, Lu L V, Pan B -C, Zhang Q -J, Zhang W -M, Zhang Q -X 2009 Critical review in adsorption kinetic models *Journal of Zhejiang University Science A* **10**(5) 716
- [21] Ho Y S 2006 Review of second order models for adsorption systems *Journal of Hazardous Material B* **136** 681
- [22] Juang R S , Chen M L 1997 Application of the Elovich equation to the kinetic of metal sorption with solvent- impregnated resins *Ind. Eng. Chem. Res* **36** 813
- [23] Idris S, Iyaka Y A, Ndamitso M M, Mohammed E B, Umar M T 2011 Evaluation of kinetic models of copper and lead uptake from dye wastewater by activated prode of Barbados shell. *American Journal of Chemistry* **1**(2) 47
- [24] Zewail T M and Yousef N S 2015 Kinetic study of heavy metal ions removal by ion exchange in batch conical air spouted bed *Alexandria Engineering Journal* **54** 83
- [25] Rahman M S, Sathasivam K V 2015 Heavy metal adsorption onto Kappaphycus sp. from aqueous solutions: The use of error functions for validation of isotherm and kinetics models *BioMed Research International* **2015** 1
- [26] Akbar N A, Abdul Aziz H and Adlan M N 2015 Iron and manganese removal from groundwater using high quality limestone. *Applied Mechanics and Materials* **802** 460