Kinetics and Equilibrium of Fe$^{3+}$ Ions Adsorption on Carbon Nanofibers

Alimin$^1$, La Agusu$^2$, L. O. Ahmad$^1$, L. O. Kadidae$^1$, L. Ramadhan$^1$, M. Nurdin$^1$, N. Isdayanti$^1$, Asria$^1$, P. Aprilia M$^1$ and Hasrudin$^1$

$^1$Department of Chemistry, Universitas Halu Oleo, Kampus Hijau Bumi Tridharma, Anduonohu-Kendari 93232, Indonesia.
$^2$Department of Physics, Universitas Halu Oleo, Kampus Hijau Bumi Tridharma, Anduonohu-Kendari 93232, Indonesia.

E-mail: alimin@uho.ac.id

Abstract. Generally, the interaction between metal ions and adsorbent is governed by many factors including; concentration of metal ions, interaction time and solution pH. In this work, we applied liquid phase adsorption for studying the interaction between Fe$^{3+}$ ions and Carbon Nanofibers (CNFs) irradiated by ultrasonic waves. Kinetics and isotherms model of the Fe$^{3+}$ ion adsorption was investigated by varying contact time and pH. We found that the Fe$^{3+}$ ions were efficiently adsorbed on CNFs for 0.5 h in acidic pH of around 5. In order to obtain the best-fitted isotherms model, Langmuir and Freundlich's isotherms were used in this work. The adsorption equilibrium Fe$^{3+}$ metal ions on CNFs tend to follow Langmuir. Adsorption kinetics of Fe$^{3+}$ ions on CNFs were investigated by using both pseudo-first and pseudo-second orders. The adsorption kinetics coincided well with the pseudo-second-order.

Keywords. Carbon nanofibers (CNFs), Fe$^{3+}$ ions, kinetics and nanofiber.

1. Introduction

Study of kinetics and equilibrium of metal ions adsorption on adsorbents such as activated carbon [1–5], modified activated carbon [6, 7] and nanocarbon [8, 9] has been intensively studied for a wide variety of purposes. Kinetics and equilibrium for iron ion removal by activated carbon have been intensively studied [1–5]. Adsorption behavior of Fe$^{2+}$ ion from aqueous solution on activated carbon has been reported [1–3]. Kinetics and thermodynamics of Fe$^{3+}$ ions adsorption onto activated carbon from biomass have been investigated by Mahmoud et al [4]. Adsorption of Fe$^{3+}$ on Acanthaceae activated carbon has been investigated [5]. In addition, modified activated carbons have been studied [6, 7]. Removal of iron from simulated contaminated groundwater using Fe$^{3+}$ impregnated activated carbon has been reported by Mondal et al [6]. Vassileva et al [7] have studied the adsorption of Fe$^{3+}$ onto ignited-based activated carbons modified by oxidation.

In the last decades, carbon nanotubes (CNTs) and carbon nanofibers (CNFs) as members of carbon family have attracted the attention of researchers because they have the large surface area, hence they are projected to be one of the promising adsorbents for adsorbing metal ions [8, 9]. Adsorption of the iron ion on the nanocarbon has been intensively reported [8, 9]. Ozcan et al [8] have applied multi-wall carbon nanotubes to remove Fe$^{3+}$ from the water. Furthermore, Abdullah et al. [9] have reported
Fe³⁺ ions removal using CNFs. However, most of those studies were addressed to remove metal ions from wastewater [1–9].

In our study, prior to producing Fe nanoparticles on CNFs through liquid phase adsorption, it was crucial to study of kinetics and equilibrium of Fe³⁺ metal ions adsorption on CNFs because the metal ions adsorption on adsorbent strongly depends on parameters such as contact time, the initial pH of the solution and the initial dose of metal ions. Based on literature review, to the best of our knowledge, not so many researchers focusing the effect of the ultrasonic wave on Fe³⁺ adsorption. Ultrasonic energy should aid adsorption of Fe³⁺ ions onto CNF during the interaction period. Therefore, in the present work, adsorption of Fe³⁺ metal ions on CNFs using liquid phase adsorption [11] was done in various sonication time and initial pH of the solution [11]. These parameters are two crucial parameters of kinetics and thermodynamics allowing for maximizing the amount of adsorbed metals. A significant amount of Fe³⁺ ions adsorbed onto CNFs is useful for producing Fe nanoparticles onto CNFs.

2. Materials and methods

The effect of contact time on the metal ions adsorption was studied by doping 5 mg of CNFs with 50 mL of 25 mg/L solution of Fe³⁺ assisted by an ultrasonic wave of 53 Hz in various times sonication (5 – 210) min. The effect of initial pH on the metal ions was studied by means doping 5 mg of CNFs with 50 mL of 25 mg/L solution of Fe³⁺ within initial pH ranging from 2 to 10 assisted by the ultrasonic energy for 30 min. All pH measurements were conducted using a pH meter (370 pH Meter Jenway) in which the initial pH levels of experimental solution were adjusted using 0.1 M solution of HCl or NaOH. The effect of initial concentration the metal ions on the adsorption was studied by means each 5 mg of CNFs was dipped ultrasonically for 30 min in different concentration of 50 mL solution of Fe³⁺ with initial pH around 5. After doping treatment, solid and filtration were separated by filtration using a 0.45 pore size Whatman membrane filter paper. The final and the initial concentrations of the metal ions infiltrate were determined by Atomic absorption Spectrophotometer (Hitachi Z-2000). The concentration of the metal ions adsorbed in CNFs was obtained from the difference between the initial and the final metal ions concentrations. Here, all the calculated parameters of adsorption equilibrium of the metal ions such as the amount of the ions, the percentage of the adsorbed ions, and adsorption isotherms refer to work in [2].

The amount of the metal ions adsorbed into CNFs at equilibrium, qₑ (mg/g) is given by:

\[
q_e = \frac{(C_o - C_e) \times V}{M}
\]

(1)

where \(C_o\) and \(C_e\) (mg/L) are the liquid phase concentrations of the metal ions at the initial and at equilibrium states, respectively; \(V\) (L) is the volume of solution; and \(M\) (g) is the mass of dried CNFs used.

The percentage of metal ions that was adsorbed in CNFs was calculated by the following Equation 2:

\[
\text{Percentage of Adsorption (\%)} = \frac{(C_o - C_e)}{C_o} \times 100
\]

(2)

where \(C_o\) and \(C_e\) (mg/L) are the liquid phase concentrations of the metal ions at the initial and at equilibrium states, respectively.

The procedure of contact time effect as adsorption kinetics aspect in this study was similar to that of batch equilibrium. However, the amount of the metal ions adsorbed in CNFs at equilibrium, \(q_e\) (mg/g) is obtained by calculating the metal ions uptake at selected time intervals. The amount of the adsorbed metal ions at any time, \(q_t\) (mg/g) was calculated by:

\[
q_t = \frac{(C_o - C_t) \times V}{M}
\]

(3)
where $C_t$ (mg/L) is the liquid phase concentration of the metal ions at any time (min). Langmuir and Freundlich's models were employed for studying adsorption isotherms. Langmuir adsorption isotherm is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{C_e}{q_m}$$  \hspace{1cm} (4)

where $C_e$ (mg/L) is the equilibrium liquid phase concentration of metal, $q_e$ (mg/g) is the number of metals adsorbed at equilibrium, $q_m$ (mg/g) is the maximum adsorption capacity and $K_L$ is Langmuir equilibrium constant. $R_L$ associated with a characteristic of Langmuir isotherm is determined by using:

$$R_L = \frac{1}{(1+q_mK_L)}$$  \hspace{1cm} (5)

Freundlich adsorption isotherm is given by:

$$\log q_e = \log q_m + \frac{1}{n} \log C_e$$  \hspace{1cm} (6)

where $C_e$ (mg/L) is the equilibrium liquid phase concentration of metal, $q_e$ (mg/g) is the number of metals adsorbed at equilibrium, $q_m$ (mg·L⁻¹)(L·g⁻¹)¹/n is Freundlich constant associated with adsorption capacity. 1/n (mg·L⁻¹) is Freundlich constant related to sorption intensity of the sorbent.

### 3. Results and discussion

The effects of sonication time and initial pH on the amount of adsorbed Fe³⁺ on CNFs are presented in Figure 1 and Figure 2, respectively.

**Figure 1.** The effect of sonication time on the amount of adsorbed Fe³⁺ on CNFs

**Figure 2.** The effect of initial pH on the amount of adsorbed Fe³⁺ on CNFs

Effect of sonication time presented in Figure 1 exhibits that the metal ions adsorptions goes quickly from the initial stage of 5 min until 20 min. At the second stage with range time of around 20 min to 30 min, the metal ions uptake becomes slower until it reaches a constant time of sonication at about 30 min. After sonication for 30 min, the metal ions adsorption tends to be constant. The fast uptake of metal ions at the initial stage might be caused by a large number of surface sites available on CNFs for adsorption of the metal ions. The next stage, at sonication time above 30 min the metal ions sorption is nearly getting constant and the rate of the adsorption is getting slower with the time due to the sites were almost entirely occupied by the adsorbate. It is possible that the bulk Fe³⁺ ions adsorbed on the surface sites and Fe³⁺ ions in solution will repulse each other. Consequently, surface sites of CNFs would not be able to adsorb Fe³⁺ metal ions anymore. Therefore, sonication time of 30 min was selected for all the subsequent experiments.

The effect of initial pH on the amount of adsorbed Fe³⁺ on CNFs is presented in Figure 2. It is well known that acidic solution contains high proton concentration with high mobility property. The H⁺
ions should compete with Fe$^{3+}$ metal ions on active sites of the adsorbent. Due to higher abundance and higher mobility of H$^+$ ions in solution, Fe$^{3+}$ ion should not be able to compete with H$^+$ ions. As a result, the amount of the adsorbed Fe$^{3+}$ ion on CNFs is relatively small [13]. It is similar to high pH of a solution having OH$^-$ high abundance. Commonly, in high pH region (above pH 7), the adsorption of metal ions decreases dramatically due to the formation of metal hydroxide.

In our study, however, we found the unusual phenomenon of the adsorption in which the metal ions uptake was relatively high even though at low pH (pH < 3.5) i.e 97.17 %. At pH range around 3.5 until 5, the adsorption of metal ions tends to increase with the increase of solution pH. The highest metal ions uptake was reached at pH 5 (98 %). At pH region above 5 the adsorption of the metal ions indeed decreases with the increase of solution pH, even though the amount of Fe$^{3+}$ uptake is still relatively high. The amount of Fe$^{3+}$ uptake at pH range of 8 to 10 is more than 93 %. The relatively high amount of Fe$^{3+}$ uptake at those pH regions might result from ultrasonic energy. Probably, the ultrasonic wave has facilitated the electrostatic attraction between the metal ions and active sites of CNFs, hence reduction of Fe$^{3+}$ to be Fe$^0$ on the active sites take place easily. The role of the ultrasonic wave on metal ions reduction on nanocarbon has been reported by the author [11]. Another possibility is the high adsorption because of the large surface area of CNFs.

In this work, Langmuir and Freundlich's models were used for studying the adsorption isotherm. Figure 3 and Figure 4 shows curves of Langmuir and Freundlich adsorption isotherms, respectively. The straight line in Figure 3 was obtained by plotting $C_e/q_e$ versus $C_e$ using Langmuir adsorption isotherm (Equation 4). The $q_m$ value was determined through the slope of the straight line (Figure 3). In this case, the slope equal to 1/$q_m$ and 1/$q_m K_L$ is defined as intercept. The characteristic of Langmuir isotherm can be evaluated from $R_L$ value as Equation 5. The equilibrium data were fitted to Langmuir isotherm. The $q_m$, $K_L$, $R^2$ and $R_L$ values as Langmuir isotherm parameters were then obtained. The values of those parameters are $q_m (347.222 \text{ mg/g})$, $K_L (9.931 \text{ L/mg})$, $R^2 (0.981)$ and $R_L (0.00029)$. The value of $R_L$ which is less than 1 indicates that Langmuir adsorption isotherm is favorable [2].

Figure 3. Langmuir adsorption isotherm

Figure 4. Freundlich adsorption isotherm

Figure 4 exhibits plot of log $q_e$ against log $C_e$. The plot gives a straight line was obtained from Freundlich adsorption isotherm (Equation 6) with a slope of 1/n and intercept of log $q_m$. The 1/n is Freundlich constant related to sorbent intensity, whereas $q_m$ is Freundlich constant associated with adsorption capacity. The Freundlich isotherm parameters are $n (0.374 \text{ mg/L})$, $q_m ((2.034 \text{ mg.g}^{-1}) (\text{L.g}^{-1})^{1/n})$, and $R^2 (0.847)$. The larger value of $q_m$ means the higher adsorption capacity of CNFs. The adsorption of Fe$^{3+}$ metal ions on CNFs is realistically described by Langmuir and Freundlich isotherms. Based on the $R^2$ values, however, Langmuir isotherm provided the better fit compared to Freundlich isotherm. It suggests that maximum adsorption of Fe$^{3+}$ metal ions occurred was covered by a monolayer of adsorbate.

In this work, two common models, namely, pseudo-first order and pseudo-second-order models employed for the modeling of the kinetics of adsorption of Fe$^{3+}$ metal ions are given by Equation 7 and Equation 8, respectively:
\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \\
\frac{t}{q_t} = \frac{1}{k_1 q_e} + \frac{t}{k_2 q_e^2} 
\]

where \( q_e \) and \( q_t \) (mg/g) are the amounts of Fe\(^{3+}\) ions uptake at equilibrium and at any time, \( t \) (h), respectively, \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g·mg\(^{-1}\)·min\(^{-1}\)) are the adsorption rate constants for the pseudo first-order and pseudo second-order models, respectively. The plot of \( \log(q_e - q_t) \) versus \( t \) gives a straight line with a slope of \( k_1 \) and intercept of \( \log q_e \) as shown in Figure 5. The values of \( k_1 \) and \( R^2 \) obtained from the plots for adsorption of the metal ions on the CNFs are 0.1221 min\(^{-1}\) and 0.9983, respectively. The plot of \( \frac{t}{q_t} \) against \( t \) provides a straight line with slope and intercept of \( \frac{t}{q_e} \) and \( \frac{1}{k_2 q_e^2} \), respectively as presented in Figure 6.

**Figure 5.** Pseudo-first order kinetic model for Fe\(^{3+}\) metal ions adsorption

**Figure 6.** Pseudo-second order kinetic model for Fe\(^{3+}\) metal ions adsorption

The values of \( k_2 \) and \( R^2 \) obtained from the plots for adsorption of the metal ions on the CNFs are 0.025441 g·mg\(^{-1}\)·min\(^{-1}\) and 1.0, respectively. In comparison, an \( R^2 \) value obtained from the pseudo-first-order slightly lower than that of the pseudo-second-order model indicating that the adsorption of Fe\(^{3+}\) metal ions on CNFs tends to follow the pseudo-second-order kinetics model. Since, our experimental data is in a good agreement with pseudo-second-order model, then the \( q_e \) value should be calculated from the slope of the graph in Figure 6. The calculated \( q_e \) is 236.967 mg/g. This value is similar to experimental \( q_e \) value i.e., 236.470 mg/g [2]. The \( q_e \) value was obtained by involving \( C_o = 25 \) mg/L, \( M = 0.05g \), \( C_e = 1.3530 \) mg/L and \( V = 0.05 \) L in Equation 1. It is important to be noted that the experimental \( q_e \) value associates with equilibrium adsorption capacity at optimum time (\( q_e \)). As a comparison, the calculated \( q_e \) value obtained from the intercept of pseudo-first-order is 0.0408 mg/g which is significantly different from the experimental value.

### 4. Conclusions

We investigated that the Fe\(^{3+}\) ions were efficiently adsorbed on CNFs for 0.5 h in acidic pH of around 5 i.e., 98 %. However, we found the unusual phenomenon of the adsorption in which the metal ions uptake was still relatively high even at low pH (pH < 3.5) i.e. 97.17 %. The finding is beneficial for producing Fe nanoparticles onto CNFs. Adsorption equilibrium of Fe\(^{3+}\) metal ions on CNFs was fitted to Langmuir while the adsorption kinetic tends to follow the pseudo-second-order.
Acknowledgments
The authors thank Directorate of Research and Community Service-The Ministry of Research, Technology and Higher Education of the Republic of Indonesia for funding this work through the Research Grant for Applied Product #065/ADD/SP2H/LT/DRPM/VIII/2017. The authors sincerely thank Professor Katsumi Kaneko of Shinshu University-Japan for supplying CNFs.

References
[1] Kouakou U, Ello A S, Yapo J A, and Trokourey A 2013 Adsorption of iron and zinc on commercial activated carbon J. Environ. Chem. Ecotoxicol 5(6) 168–171
[2] Alslaibi T M, Abustan I, Ahmad M A, and Foul A A 2013 Desalination and Water Treatment
[3] Thilagam G, Mani N, Arivoi S, and Hema M 2016 Adsorption behavior of Fe (II) ion from aqueous solution onto nano carbon International Journal of Chemical Studies, 4(1) 96–102
[4] Mahmoud M A, Gawad E A, Hamoda E A, and Haggag E A 2015 Kinetics and thermodynamic of Fe(III) adsorption type onto acti-vated carbon from biomass: kinetics and thermodynamicsstudies ESAIJ 11(4) 128–136
[5] Hussain A A, Mohammed S R, Nallu M, and Arivoli S 2012 Adsorption of Fe(III) from aqueous solution by acanthaceae activated carbon J. Chem. Pharm. Res. 4(4) 2325–2336
[6] Mondal P, Balomajumder C, and Mohanty B 2007 A laboratory study for the treatment of arsenic, iron, and manganese bearing ground water using Fe(3+) impregnated activated carbon: effects of shaking time, pH and temperature Journal of Hazardous Materials 144 420–426
[7] Vassileva P St and Detcheva A K 2010 Adsorption of some transition metal irons [Cu(II), Fe(III), Cr(III) and Au (III)] onto Lignite-Based Activated Carbons Modified by Oxidation Adsorption Science & Technology 28(3)
[8] Ozcan S G, Satiroglu N, and Soylak M 2010 Column solid phase extraction of iron(III), copper(II), manganese(II) and lead(II) ions food and water samples on multi-walled carbon nanotubes Food and Chemical Toxicology 48 2401–2406
[9] Abdullah N, Rinaldi A, and Hamid S B A 2015 Synthesis and Adsorption Performance of Carbon Materials for the Removal of Iron (III) from Aqueous Solution Applied Mechanics and Materials 699 988–993
[10] Huang F, Xu Y, Liao S, Yang D, Hsieh Y L, and Wei Q 2013 Preparation of Amidoxime Polyacrylonitrile Chelating Nanofibers and Their Application for Adsorption of Metal Ions Materials 6 969–980
[11] Alimin A, Narsito N, Kartini I, and Santosa S J 2015 Production of Silver Nanoparticle Chains inside Single Wall Carbon Nanotube with a Simple Liquid Phase Adsorption Bulletin of Chemical Reaction Engineering & Catalysis 10(3) 266–274
[12] Hameed B, and M El–Khaiary 2008 Equilibrium, kinetics and mechanism of malachite green adsorption on activated carbon prepared from bamboo by K2CO3 activation and subsequent gasification with CO2 J. Hazard. Mater. 157 344–351
[13] Boz’ic´D, Stankovic´V, Gorgievski M, and Bogdanovic’G 2009 Adsorption of heavy metal ions by sawdust of deciduous trees J. Hazard. Mater. 171 684–692