CHAPTER VII

KINETICS, AND ISOTHERM OF CYANIDE ADSORPTION USING NANO ZERO-VALENT IRON COATED ON DIATOMITE

Nano zerovalent iron coated on diatomite (nZVI-D_2) is an effective adsorbent for removing various organic and inorganic contaminants. In this study, nZVI-$D_2$was used to investigate the removal of cyanide in the concentration range of 25-175 mg/L. The nZVI-D_2can uptake of cyanide more than 99% at initial concentration 25-50 mg/L. Langmuir and Freundlich models are the most common isotherms for correlating adsorption experimental data though other isotherms. The maximum adsorption capacity of nZVI-$D_2$for cyanide removal was found to be 134.016 mg/g. The calculated activation energy for adsorption was 78.12 kJ/mol from D–R isotherm, indicating that the adsorption process to be chemisorption. The adsorption kinetics well fitted using a pseudo second-order kinetic model shown that adsorption process appeared to be controlled by chemical process. The intraparticle diffusion model described that the intraparticle diffusion was not the only rate-limiting step. Therefore the overall adsorption process was controlled by chemisorption, film diffusion and intra-particle diffusion in nature. These results suggested that nZVI-D_2 could be employed as an efficient adsorbent for the removal of cyanide from contaminated water sources.

7.1 Introduction

Cyanide is a highly toxic compound species which is discharged into the environment through the wastewater of industrial activities such as gold refining, metal plating, photography industry, electronics, coal coking, chemical manufacturing and steel industries, chemical fertilizer and mining (Gupta, Balomajumder, & Agarwal, 2012; Moussavi & Khosravi, 2010; Saxena, Prasad, Amritphale, & Chandra,

---

This paper is accepted to published in the journal Environmental Progress & Sustainable Energy

2001). The release of cyanide from industries worldwide has been measured more than 14 million kg/yr (Gupta et al., 2012). The cyanide species in wastewaters contains i.e. free, metal–cyanides and cyanide related compounds. The wastewater has been contained by cyanide and cyanate compounds as serious hazardous substances due to their strong effects on both the environment and human (Sirianuntapiboon, Chairattanawan, & Rarunroeng, 2008). The US-health service cites 0.2 mg/L as permissible limit for cyanide in wastewater.

A chemical oxidation and coagulation are used to treat wastewater due to the high concentration of cyanide compound (Barnes, Wright, Graham, & Jones-Watson, 2000; Yazıcı, Deveci, & Alp, 2009), but it gave a large amount of hazardous sludge. While, a biodegradation is usually the good method for treating wastewater because it's low cost and non-toxic for environment (Kaewkannetra, Imai, Garcia-Garcia, & Chiu, 2009). However, the biodegradation process use to the long time in the cyanide and cyanide removal. Several researchers study to apply the adsorption process to remove and degrade cyanide compounds from the wastewaters. In addition, adsorption is a widely used technology for the removal and recovery of cyanide. The treatment method which is requiring air or oxygen in the solution resulting cyanide is oxidized to cyanate (Dash, Balomajumder, & Kumar, 2009).

Among these methods, chemical reduction and adsorption by nano zero-valent iron (nZVI) is the high reactivity and relatively large surface area because it is a small particle with average particle size 10-100 nm and a specific surface area of 20-25 m^2/g. Iron in oxidation state zero is very unstable, thus reactive and represents one of the strongest reducers. However, the applications of nZVI have problems, such as the toxic substance or nZVI release into the environment, aggregation of nZVI particles and the nZVI made to pressure drop in the system. Hence, supporting materials have been used to immobilize nZVI (Arshadi, Soleymanzadeh, Salvacion, & SalimiVahid, 2014; Chen et al., 2013; Fu et al., 2013). Among the supports, synthesized zeolite showed a good adsorption performance; however, it disadvantages because the cost of preparation was very high. Since, diatomite ($SiO_2 \cdot nH_2O$) is a kind of natural zeolite, soft and lightweight with porous structure. It provides many unique properties, such as high porosity (80-90% voids), high surface area and chemical inertness and it is widely used as filter agents, catalyst carriers. Therefore, in this study will use nano zero-valent iron supported on diatomite (nZVI-D) to treat cyanide.

7.2 Objectives

The objective of this research is study the influence of various experimental parameters on cyanide adsorption and determined the optimum adsorption conditions. The adsorption kinetics and isotherm models is investigated to develop an understanding of controlling reaction pathways and used to quantify the adsorptive capacity of an adsorbent. All of all, the goal of this study was to develop the adsorbent which have low cost and efficient in the removal cyanide.

7.3 Materials and methods

7.3.1 Materials

All reagents including sodium cyanide (NaCN, Panreac; UK), iron(III) sulphate ($FeSO_4{\cdot}7H_2O$, Ajax Finechem; Australia), sodium borohydride ($NaBH_4$, Rankem; India), ammonium hydroxide (NH_4OH, Panreac; Barcelona) and hydrogen chloride (HCl_2, RCL Labscan; Thailand) were analytical grade. A Stock solution of cyanide was prepared by dissolving 1 g NaCN into distilled water, acquired 1,000 mg/L of cyanide solution. The concentration range of cyanide was prepared from stock solution varied between 25 and 175 mg/L. The sample of diatomite was achieved from the North of Thailand. The diatomite was washed with distilled water and dried at 110°C in a drying oven for 24 h. Then, it was kept in the polyethylene bags.

7.3.2 Batch experiments for adsorption of cyanide by nZVI-D

The rate of cyanide (120 mL, 25 to 175 mg/L) removal from solution containing 0.75 g/L of the nZVI-$D_2$was monitored as a time course during 0-180 min. The suspensions were filtered with syringe Filter Nylon 0.45 µm membrane (Lubitech, Thailand). Cyanide concentration is measured by kolorimetrisch method and colorimetric method by cyanid test and cyanide test (Merck, Germany). The percentage cyanide removal was defined using the following equation:

$$Y = \frac{C_0 - C_t}{C_0} \times 100 \tag{2.20}$$

where C_0 is the initial concentration of cyanide (mg/L) and C_t is the concentration of cyanide (mg/L) after adsorption at time. *Y* is the percentage of removal heavy metal.

The adsorption capacity, q_e (mg/g), was determined as follows:

$$q_e = \frac{\left(C_0 - C_e\right)}{M} V \tag{4.1}$$

where C_o and C_e are the initial and equilibrium solution concentrations (mg/L), respectively; *V* is the volume of the solution (L); and *M* is mass of adsorbent (g).

7.3.3 Adsorption isotherm models of cyanide

Several adsorption isotherms were used for explain the correlate adsorption equilibrium between adsorbent and heavy metal solution. Adsorption of cyanide by nZVI-D$_2$ was modeled using five adsorption isotherms, namely, Langmuir, Freundlich, Dubinin-Radushkevich, Tempkin and Harkin's - Jura isotherm were tested. The equation for Langmuir, Freundlich, Dubinin-Radushkevich model could be described as Eq. (2.3, 2.5, 2.6) respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \tag{2.3}$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{2.5}$$

$$\ln q_e = \ln q_d - \beta \varepsilon^2 \tag{2.6}$$

The Tempkin isotherm model considered that the effect of adsorbate interactions on adsorption and interactions the heat of adsorption of all the molecules in the layer. The Tempkin isotherm is applied in the following form

$$q_e = \frac{RT}{b} \ln\left(A_T C_e\right) \tag{7.1}$$

where q_e is the adsorbed amount at equilibrium (mg/g), C_e is the adsorbent equilibrium concentration (mg/L). A_T and *b* are the Tempkin isotherm constants.

The Harkin's - Jura isotherm assumes multilayer adsorption which can be explained with the existence of a heterogeneous pore distribution (Başar, 2006; Gürses et al., 2004). The Harkin's-Jura isotherm is expressed as

$$\frac{1}{q_e^2} = \frac{B}{A} - \left(\frac{1}{A} \left(\log C_e \right) \right) \tag{7.2}$$

where, q_e is the adsorbed amount at equilibrium (mg/g), C_e is the adsorbent equilibrium concentration (mg/L). *A* and *B* are the Harkin's - Jura isotherm constants.

7.3.4 Kinetic adsorption isotherms of cyanide

The three kinetic models, pseudo first-order, pseudo second-order and intra-particle diffusion models were fit experimental data to examine the adsorption kinetics of cyanide removal by nZVI-D_2. They used to study the examination of the controlling mechanisms of adsorption process as chemical reaction, diffusion control, and mass transfer.

Pseudo first-order kinetic model is the earliest known one describing the adsorption rate based on solid capacity. It is generally expressed as follows:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303} t \tag{2.9}$$

where q_e and q_t are the adsorption capacity at equilibrium and at any time *t*, respectively (mg/g), and k_1 is the rate constant of pseudo first-order adsorption (min^{-1}).

Pseudo second-order kinetic model based on solid phase adsorption which is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2.10}$$

where k_2 (g/mg·min) is the pseudo second-order rate constant of adsorption.

Intraparticle diffusion model explored intraparticle diffusion resistance affecting adsorption which is generally represented as follows:

$$q_t = k_i t^{1/2} \tag{2.12}$$

where k_i (mg/g·min$^{1/2}$) is the intraparticle diffusion rate constant

7.4 Results and discussion

7.4.1 Effect of contact time and initial concentration of cyanide adsorption

The equilibrium time and initial concentration is one of the most important parameters to adsorption heavy metal. The effect of contact time and initial concentration on removal of cyanide was display in Fig 7.1 (a-b). The removal of cyanide increased rapidly in first 30 min and afterward increased slowly between 30-180 min. However, the adsorption equilibrium time of cyanide removal onto nZVI-D_2 was found at 120 min because of the percentage removal constant. The uptake of cyanide was 88.00% at 50 min and 99.64% at 100 min by nZVI-D_2.

Fid 7.1a showed the percentage removal of cyanide decreased from 99.82% to 57.14% for initial concentration increased 50-175 mg/g. The percentage removal was decreased because of the lack of available active sites on the surface of adsorbents which are required for the high initial concentration of cyanide. Nevertheless, the equilibrium time for initial lead concentrations of 25-50 mg/L was only 10 min, while it became 30 min when the initial lead concentration was raised to 100–175 mg/L. The initial concentration in the range of 25-50 mg/L was adsorbed completely because nZVI-D_2 has active site more than enough. The possible reason, the initial lead concentration increased while the number of active site is constant, the active sites are not able to adsorb all cyanide in solution immediately. Therefore, it needs more time to fill up the active sites. Whereas, the adsorption was very fast in low concentration because of the solutions uncovered the surface and active sites on the adsorbents. On the contrary, the high concentration, the surface and active sites was full covered, the adsorption was slowly. Normally, the higher concentrations of cyanide were affected the slower rate and lower efficiency of cyanide removal from aqueous solution. However, the initial concentration has an important driving force to overcome all mass transfer resistance of cyanide between the aqueous and nZVI-D_2. Therefore a high initial concentration of cyanide can be increased the adsorption capacity (Ozmen et al., 2010).

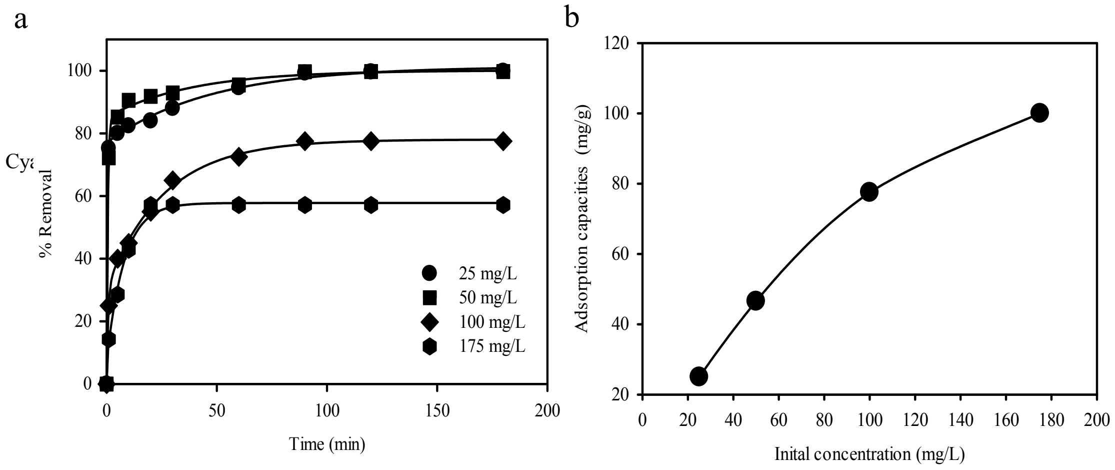

Figure 7.1 Cyanide removal as a function of adsorption time at different initial cyanide concentrations. (a) percentages removal (b) adsorption capacity at 0.75 g/L of the nZVI-D_2, pH 6 and 30 °C

The adsorption capacity of cyanide was shown in Fig7.1b. It can be seen that the adsorption capacity was increased when initial concentration increase. In other words, the initial concentration increased from 25 to 50 mg/L resulting that the adsorption capacity was increased 100 %. Conversely, initial concentration increased from 100 to 175 mg/L getting that the adsorption capacity was only increased 25 %. This may be due to the cyanide not complete use of active site of the adsorbent in the low concentration because the surface area and active site was abundantly available. This may indicate that the adsorption is limited by number of the available active sites which are not sufficient for the high initial concentration of the cyanide. Another reason was mass transfer of cyanide solution into the surface and active site of nZVI-D_2 which the combination affected for the removal cyanide.

7.4.2 Adsorption isotherm models of cyanide

The Langmuir, Freundlich, Dubinin-Radushkevich, Tempkin, and Harkin's-Jura adsorption isotherm models were used to study the surface characteristics of the adsorbent and adsorption characteristics using relatively range of cyanide concentrations (25-175 mg/g). The isotherm model describe the adsorption process was choose by the correlation coefficients (R^2). The correlation coefficients for the linear regression fit of Langmuir model ($R^2 = 0.991$) were found to be higher than those of Freundlich, Dubinin-Radushkevich, Tempkin, and Harkin's-Jura adsorption isotherm models respectively, shown in Fig 7.2(a-d). The Langmuir model assumes monolayer adsorption of adsorbate onto adsorbent surface and interaction between the adsorbed molecules and adsorption sites having uniform energies (Anirudhan, Divya, & Suchithra, 2009; Baysal, Çinar, Bulut, Alkan, & Dogru, 2009; Behnamfard & Salarirad, 2009). The removal of cyanide was trial at pH 6 because the surface charge of nZVI-D_2 was positive ions. It can be explained that positive charges of nZVI-D_2 are generated on its surface due to chemosorption, as well as complexion reactions occur heterogeneous surface adsorption and monolayer adsorption (Hong, Kim, Baek, & Yang, 2008). The results of study were as well as the investigation of Moussavi and Khosravi (Moussavi & Khosravi, 2010). The maximum adsorption capacities (q_{max}) were determined as 134.01 mg/g. Depci (Depci, 2012) reported that the maximum monolayer adsorption capacities for cyanide onto lignite-activated carbon (LAC) and iron-impregnated activated carbon (FeAC) were found as 60.18 mg/g and 67.82 mg/g at pH values of 7–7.5, respectively. In another study, Gupta, Balomajumder, & Agarwal (Gupta, Balomajumder, & Agarwal, 2012) described that the Langmuir adsorption capacities for cyanide onto pressmud surface was determined to be 10.6 mg/g. Therefore, the nZVI-D_2 can be adsorbing cyanide more than LAC, FeAC and pressmud surface. To determine if adsorption process is favorable or unfavorable, for the Langmuir type adsorption process, isotherm can be classified by a term R_L, a dimensionless constant separation factor, which is defined as below:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (2.4)$$

Value of R_L < 1 represents the favorable adsorption and value greater than one represents unfavorable adsorption. The values of R_L were found in the range of 0.013-0.049, indicating that the adsorption is favorable.

Furthermore, the Freundlich isotherm (R^2 = 0.977) supposed the cyanide adsorbs onto the heterogeneous surface of an adsorbent (Boparai, Joseph, & O'Carroll, 2011; El-Aila, Elsousy, & Hartany, n.d.; Moussavi & Khosravi, 2010). Value of n more than 1 (6.398) represents a favorable adsorption condition.

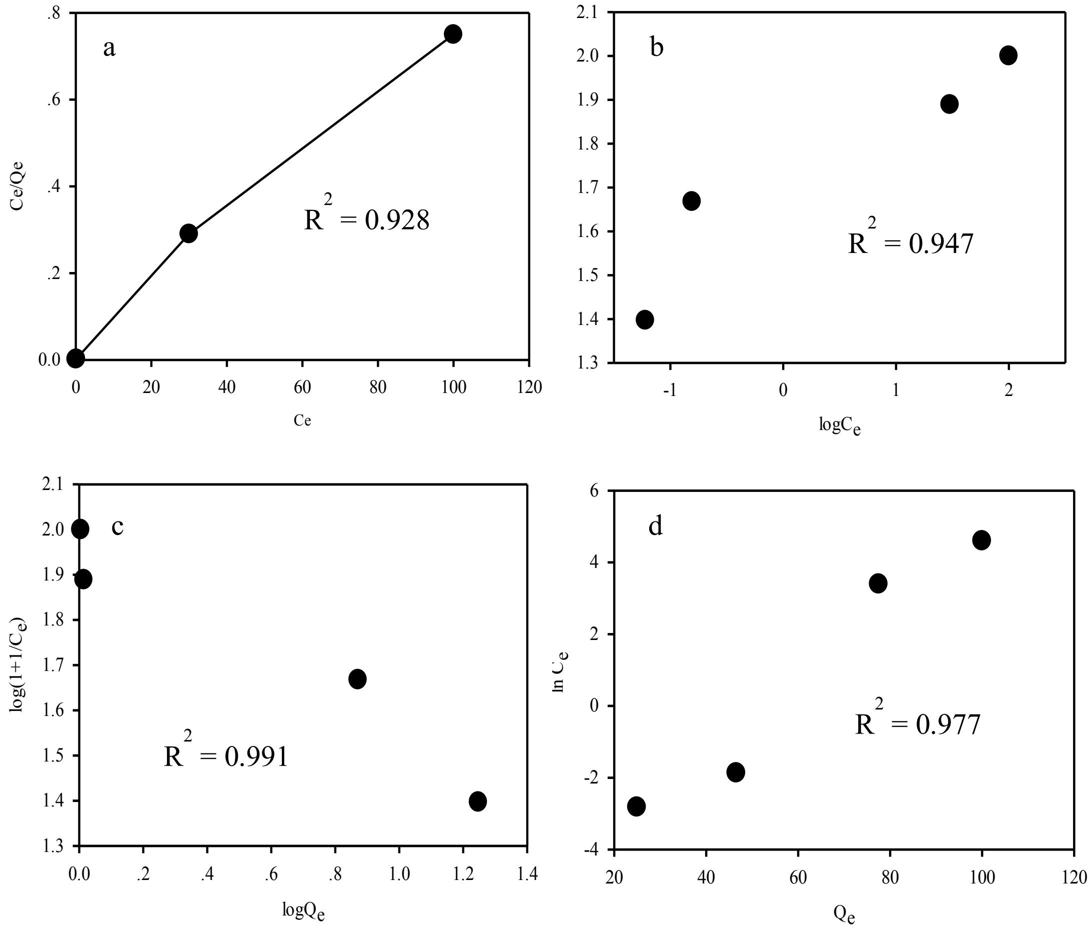

Figure 7.2 (a) Langmuir, (b) Freundlich, (c) Dubinin–Radushkevich, and (d) Temkin isotherm model for cyanide adsorption on nZVI-D_2 at 0.75 g/L of the nZVI-D, pH 6 and 30°C

In addition, heat of adsorption between cyanide-nZVI-D_2 interactions on adsorption isotherms were considered by Temkin isotherm model. It shown that the variation of adsorption energy was 289.81 kJ/mol, which shown that the adsorption processes was exothermic that is also evaluated by Langmuir model (Boparai et al., 2011) and considered chemisorption of an adsorbate onto the adsorbent (Boparai, Joseph, & O'Carroll, 2011). Furthermore, the constant in D–R isotherm gives the mean free energy (*E*) of adsorption per molecule of cyanide when it transferred to the surface of the nZVI-D_2 from infinity in the solution (Hutson & Yang, 1997). The value *E* is equals to 78.12 kJ/mol which indicating that the chemical ion exchange mechanism was involved in the adsorption process (Febrianto et al., 2009). On the other hand, the research of Gupta, Balomajumder, & Agarwal (Gupta et al., 2012) was found the value *E* is equals to 29.4 kJ/mol signified that a physical electrostatic force and chemical ion exchange mechanism was potentially involved in the sorption process. However, Harkins–Jura isotherms was not fit for correlating adsorption experimental data (R^2 = 0.445). I think that the process adsorption of cyanide by nZVI-D_2 not includes with multilayer adsorption which explained with the existence of a heterogeneous pore distribution.

Table 7.1 Several isotherm model parameters and correlation coefficients for adsorption of cyanide on nZVI-D_2

adsorption isotherm	parameter	numerical value	R^2
Langmuir	q_{max} (mg/g)	134.016	0.991
	K_L (L/mg)	0.408	
	R_L	0.013-0.049	
Freundlich	K_F (L/g)	48.089	0.977
	n	6.398	
Dubinin–Radushkevich	K_D x10^{-5}	8.192	0.928
	E (kJ/mol)	78.122	
Temkin	K_T	558.317	0.949
	b (kJ/mol)	289.809	
Harkin's-Jura	A	4926.108	0.445
	B	3.448	

It is clear that, the adsorption process of cyanide with nZVI-D_2 was monolayer adsorption, chemosorption and exothermic which shown that nZVI-D_2 can freeze cyanide on the surface very well. The parameters and correlation coefficients for adsorption were shown in Table 7.1.

7.4.3 Kinetic adsorption isotherms of cyanide

The pseudo-first order kinetic model, pseudo-second order kinetic model and intra-particle diffusion models were used to predict the mechanism involved in the adsorption process of cyanide at initial concentration ranges (25-175 mg/g) which the data display in Table 7.2.

Table 7.2 Kinetic parameters for the adsorption of cyanide onto nZVI-D_2 at the different concentrations

C_o (mg/L)	**25**	**50**	**100**	**175**
$q_{e,exp}$ (mg/g)	**24.95**	**46.55**	**77.50**	**100.00**
pseudo-first-order kinetic				
$q_{e,cal}$ (mg/g)	9.92	16.13	23.06	93.60
$k_1 \times 10^{-2}$ (L/min)	0.83	1.12	0.79	2.48
R^2	0.939	0.836	0.956	0.987
pseudo-second-order kinetic				
$q_{e,cal}$ (mg/g)	25.20	41.49	80.00	102.00
$k_2 \times 10^{-3}$ (g/mg·min)	0.194	0.235	2.57	4.95
R^2	0.999	0.999	0.998	0.999
intraparticle diffusion				
k_{i1}(mmol·mg·min$^{1/2}$)	0.658	1.967	8.504	17.893
k_{i2} (mmol·mg·min$^{1/2}$)	0.206	0.306	0.768	1

The plot of t/q_t against t is shown in Fig. 7.3. The fitting of kinetic data in second order rate expression shows well linearity with high correlation coefficient (R^2 = 0.999) at the initial concentration range of 25-175 mg/L. The value of correlation coefficient for pseudo second-order kinetic model is much higher than the pseudo first-order model. Also the theoretical q_e values for cyanide adsorption (102 mg/g) was very closed to the experimental value (100 mg/g) with the pseudo-second order model at initial concentration 175 mg/g and contact time 180 min. The results showed that the pseudo second-order adsorption mechanism was predominant and the overall rate of cyanide adsorption process appeared to be controlled by chemical process (Boparai, Joseph, & O'Carroll, 2011; Febrianto et al., 2009) involving valence forces through sharing of electrons between nZVI-D_2 and cyanide. To sum up, cyanide adsorption were adsorbed onto the nZVI-D_2 by chemical interaction. Cyanide was adsorbed with nZVI-D_2 which has a stable chemical and physical properties resulting not cause secondary pollution to environment.

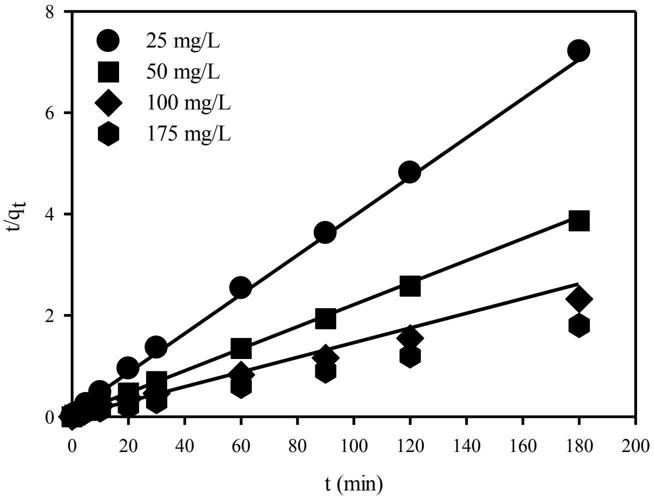

Figure 7.3 Pseudo second-order kinetics model of cyanide adsorption on nZVI-D_2 at 0.75 g/L of the nZVI-D, pH 6 and 30°C

The rate constant of pseudo second-order adsorption (k_2) was a complex coefficient and a basis of the mass transfer between adsorbate and adsorbent surface. The values of k_2 increased with increasing of the initial cyanide concentration which suggested that the enhancement of the diffusion in the solid phase and adsorption rate. In addition, initial concentration increase resulting that the mass transfer enhanced of cyanide from solution to nZVI-D_2 surface, which accelerated up the rate of cyanide removal.

The cyanide transport from the solution to the surface of the nZVI-D_2 take places in several steps. The overall adsorption process may be controlled by one or a mixture of more than one step (e.g., film diffusion, pore diffusion, surface diffusion and adsorption on the pore surface). Therefore, in this study interests the intra-particle diffusion of the metal ion from the outer surface into the pores of the adsorbent material. Intra-particle diffusion model was the line plot of q_t versus $t^{1/2}$ not passes through the origin shown in Fig 7.4, implying the intra-particle diffusion only was not the rate-limiting step. The plots present multi-linearity, indicating that two slope occurs. The first slope casing the time interval between 1 and 10 min, which has a very sharp, is ascribed to the diffusion of cyanide through the solution film to the external surface of nZVI-D$_2$ (mass transfer). The second slope (after 10 h) is defined as the slow adsorption limited by diffusion of cyanide into pores of nZVI-D$_2$ particles and forward the pores walls (intraparticle diffusion) (Depci, 2012). In addition, low concentration could be adsorbed by adsorbent sites. At high cyanide concentration, diffusion of cyanide through the film to external surface of the nZVI-D$_2$ are very fast in 10 min and then decreases following reaction time (Behnamfard & Salarirad, 2009; Dash, Balomajumder, & Kumar, 2009). Therefore, the adsorption process of cyanide on nZVI-D$_2$ was controlled by both intra-particle diffusion and mass transfer (film diffusion). To sum up, the adsorption isotherm model and kinetic adsorption isotherms of adsorption cyanide was controlled by the chemical adsorption involving between functional groups present on the adsorbent surface and the metal ions or valence forces through sharing of electrons between nZVI-D$_2$ and cyanide, film diffusion and intra-particle diffusion.

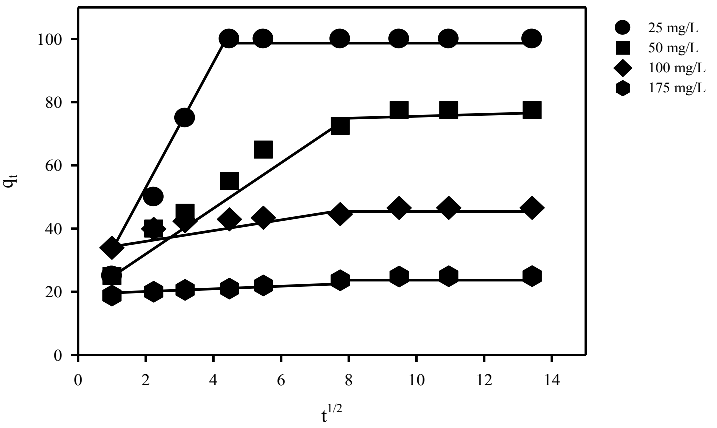

Figure 7.4 Intra-particle diffusion kinetic model of cyanide adsorption on nZVI-D$_2$ at 0.75 g/L of the nZVI-D, pH 6 and 30°C

7.4.4 Adsorption mechanism of cyanide

Adsorption mechanism of cyanide could be explained using electrostatic attraction and protonation or deprotanation of iron oxide into hydrogen ion shown in Eq 7.3-7.4 and precipitation on the surface of nZVI-D_2 and diatomite which consist of iron oxide display in Eq 7.5-7.7.

$$Fe_s\text{- }OH + H^+ \rightleftharpoons Fe_s\text{- }OH_2^+ \tag{7.3}$$

$$Fe_s\text{- }OH \rightleftharpoons H^+ + Fe_s\text{- }O^- \tag{7.4}$$

$$6CN^- + Fe^{2+} \rightarrow Fe(CN)_6^{4-} \tag{7.5}$$

$$6CN^- + Fe^{3+} \rightarrow Fe(CN)_6^{3-} + H_2O \tag{7.6}$$

$$Fe(CN)_6^{4-} + 2Fe^+ \rightarrow Fe_2Fe(CN)_6 \tag{7.7}$$

While, HCN and CN^- present in the aqueous solution at the pH values in the range of 6–8 which the removal possesses in this research used pH 6. Besides, HCN and CN are completely dissociated to CN− at a solution pH of 6. The nZVI-D_2 surface displays positive ion at pH solution below pH_{pzc} resulting that occurring the removal cyanide by electrostatics attraction force between ions of cyanide and the surface of nZVI-D. The previous research (Depci, 2012) found that activated carbon or silica is impregnated with transitional metal, the percentage removal was increased due to chemisorption and the catalytic oxidation of cyanide. Furthermore, nZVI-D_2 worked both as an adsorbent and as a carrier of catalyst for cyanide oxidation. In the presence of dissolved oxygen, the adsorbed cyanide may be oxidized to CNO^- (Eq.7.8) which was hydrolyzed to NH_4^+ (Eq. 7.9); further oxidation of CNO^- to form N_2 (Eq. 7.10) (Bernardin, 1973; Yazıcı, Deveci, & Alp, 2009; Zhang, Liu, Lv, Li, & Ying, 2010).

$$CN^- + 0.5O_2 \rightarrow CNO^- \tag{7.8}$$

$$CNO^- + 2H_3O^+ \rightarrow NH_4^+ + H_2O \tag{7.9}$$

$$2CNO^- + 1.5O_2 + H_2O \rightarrow N_2 + 2CO_2 + 2OH^- \tag{7.10}$$

It is obverse that the removal was the primary mechanism of cyanide removal; catalytic oxidation, electrostatic attraction and precipitation of the adsorbed cyanide on nZVI-D_2 shown in Fig 7.5.

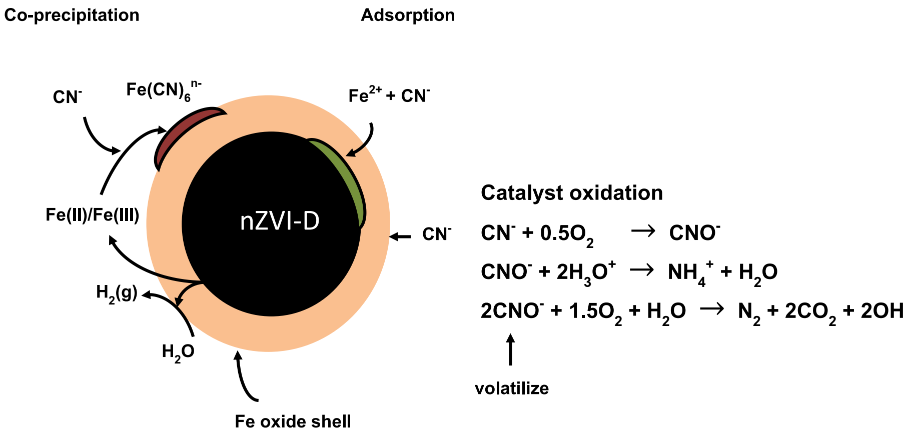

Figure 7.5 Mechanism of cyanide removal by using nZVI-D_2

7.5 Conclusions

The results of this research show that nano zero-valent iron supported on diatomite (nZVI-D_2) has an appropriate removed of cyanide from aqueous solutions. The percentage removal of cyanide decreased when initial concentration increased while the percentage removal increased when reaction time increased. The initial concentration at 25 mg/g, nZVI-D_2 can uptake of cyanide was 88.00% at 50 min and 99.64% at 100 min. The Langmuir isotherm showed a better fit than the Freundlich isotherm, thus, indicating the applicability of monolayer coverage of cadmium on nZVI surface. The maximum adsorption capacity was determined as 134.01 mg/g. In addition, the Temkin isotherm model was shown that the adsorption processes was exothermic and the mechanism process related with chemical ion exchange. The pseudo second order kinetic model described accurately the adsorption kinetics which indicating that the overall rate of cyanide adsorption process appeared to be controlled by chemical process. The values of k_2 increase with increasing of the initial cyanide concentration which suggested that the enhancement of the diffusion in the solid phase and adsorption rate. To sum up, the adsorption mechanism was found to be chemisorption and the rate-limiting step was mainly surface adsorption. Results from this study concluded that nZVI-D_2 was a well effective adsorbent for removal cyanide.

7.6 List of abbreviations

Y	percentages cyanide removal
β	a constant related to adsorption energy
ε	Polanyi potential
A	Harkin's - Jura isotherm constants
A_T	Tempkin isotherm constants
B	Harkin's - Jura isotherm constants
b	Tempkin isotherm constants
C_e	equilibrium solution concentrations (mg/L)
C_o	initial solution concentrations (mg/L)
E	mean adsorption energy (kJ/mol)
k_1	rate constant of pseudo first-order adsorption (min^{-1})
k_2	rate constant of pseudo-second-order adsorption (g/mg·min)
k_F	Freundlich adsorption constant (L/g)
k_i	intraparticle diffusion rate constant ($\mathrm{mg/g{\cdot}min}^{1/2}$)
k_L	Langmuir constant
q_e	adsorption capacity at equilibrium (mg/g)
M	mass of adsorbent (g)
n	an indication of how favorable the adsorption process
q_{max}	adsorption capacity at equilibrium for Langmuir (mg/g)
q_d	Dubinin-Radushkevich monolayer capacity (mg/g)
q_t	adsorption capacity at any time (mg/g)
R_L	dimensionless separation factor of Langmuir adsorption
V	volume of the solution (L)

7.7 References

Anirudhan, T.S., Divya, L., & Suchithra, P.S. (2009). Kinetic and equilibrium characterization of uranium(VI) adsorption onto carboxylate-functionalized poly(hydroxyethylmethacrylate)-grafted lignocellulosics. **Journal of Environmental Management, 90**(1), 549–560.

Arshadi, M., Soleymanzadeh, M., Salvacion, J.W.L., & SalimiVahid, F. (2014). Nanoscale Zero-Valent Iron (NZVI) supported on sineguelas waste for Pb(II) removal from aqueous solution: kinetics, thermodynamic and mechanism. **Journal of Colloid and Interface Science, 426,** 241–251.

Barnes, D.E., Wright, P.J., Graham, S.M., & Jones-Watson, E.A. (2000). Techniques for the Determination of Cyanide in a Process Environment: A Review. **Geostandards Newsletter, 24**(2), 183–195.

Başar, C.A. (2006). Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot. **Journal of Hazardous Materials, 135**(1–3), 232–241.

Baysal, Z., Çinar, E., Bulut, Y., Alkan, H., & Dogru, M. (2009). Equilibrium and thermodynamic studies on biosorption of Pb(II) onto Candida albicans biomass. **Journal of Hazardous Materials, 161**(1), 62–67.

Behnamfard, A., & Salarirad, M.M. (2009). Equilibrium and kinetic studies on free cyanide adsorption from aqueous solution by activated carbon. **Journal of Hazardous Materials, 170**(1), 127–133.

Bernardin, F.E. (1973). Cyanide Detoxification Using Adsorption and Catalytic Oxidation on Granular Activated Carbon. **Journal (Water Pollution Control Federation), 45**(2), 221–231.

Boparai, H.K., Joseph, M., & O'Carroll, D.M. (2011). Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. **Journal of Hazardous Materials, 186**(1), 458–465.

Chen, Z., Wang, T., Jin, X., Chen, Z., Megharaj, M., & Naidu, R. (2013). Multifunctional kaolinite-supported nanoscale zero-valent iron used for the adsorption and degradation of crystal violet in aqueous solution. **Journal of Colloid and Interface Science, 398,** 59–66.

Dash, R.R., Balomajumder, C., & Kumar, A. (2009). Removal of cyanide from water and wastewater using granular activated carbon. **Chemical Engineering Journal, 146**(3), 408–413.

Depci, T. (2012). Comparison of activated carbon and iron impregnated activated carbon derived from Gölbaşı lignite to remove cyanide from water. **Chemical Engineering Journal, 181-182,** 467–478.

El-Aila, H.J., Elsousy, K.M., & Hartany, K.A. [n.d.]. Kinetics, equilibrium, and isotherm of the adsorption of cyanide by MDFSD. **Arabian Journal of Chemistry.**

Febrianto, J., Kosasih, A.N., Sunarso, J., Ju, Y.H., Indraswati, N., & Ismadji, S. (2009a). Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. **Journal of Hazardous Materials, 162**(2-3), 616–645.

Febrianto, J., Kosasih, A.N., Sunarso, J., Ju, YH., Indraswati, N., & Ismadji, S. (2009b). Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. **Journal of Hazardous Materials, 162**(2-3), 616–645.

Fu, F., Ma, J., Xie, L., Tang, B., Han, W., & Lin, S. (2013). Chromium removal using resin supported nanoscale zero-valent iron. **Journal of Environmental Management, 128,** 822–827.

Gupta, N., Balomajumder, C., & Agarwal, V.K. (2012). Adsorption of cyanide ion on pressmud surface: A modeling approach. **Chemical Engineering Journal, 191,** 548–556.

Gürses, A., Karaca, S., Doğar, Ç., Bayrak, R., Açıkyıldız, M., & Yalçın, M. (2004). Determination of adsorptive properties of clay/water system: methylene blue sorption. **Journal of Colloid and Interface Science, 269**(2), 310–314.

Hong, H., Kim, H., Baek, K., & Yang, J.W. (2008). Removal of arsenate, chromate and ferricyanide by cationic surfactant modified powdered activated carbon. **Desalination, 223**(1–3), 221–228.

Hutson, N.D., & Yang, R.T. (1997). Theoretical basis for the Dubinin-Radushkevitch (D-R) adsorption isotherm equation. **Adsorption, 3**(3), 189–195.

Kaewkannetra, P., Imai, T., Garcia-Garcia, F.J., & Chiu, T.Y. (2009). Cyanide removal from cassava mill wastewater using Azotobactor vinelandii TISTR 1094 with mixed microorganisms in activated sludge treatment system. **Journal of Hazardous Materials, 172**(1), 224–228.

Moussavi, G., & Khosravi, R. (2010). Removal of cyanide from wastewater by adsorption onto pistachio hull wastes: Parametric experiments, kinetics and equilibrium analysis. **Journal of Hazardous Materials, 183**(1–3), 724–730.

Ozmen, M., Can, K., Arslan, G., Tor, A., Cengeloglu, Y., & Ersoz, M. (2010). Adsorption of Cu(II) from aqueous solution by using modified Fe_3O_4 magnetic nanoparticles. **Desalination, 254**(1–3), 162–169.

Saxena, S., Prasad, M., Amritphale, S.S., & Chandra, N. (2001). Adsorption of cyanide from aqueous solutions at pyrophyllite surface. **Separation and Purification Technology, 24**(1–2), 263–270.

Sirianuntapiboon, S., Chairattanawan, K., & Rarunroeng, M. (2008). Biological removal of cyanide compounds from electroplating wastewater (EPWW) by sequencing batch reactor (SBR) system. **Journal of Hazardous Materials, 154**(1–3), 526–534.

Yazıcı, E.Y., Deveci, H., & Alp, İ. (2009). Treatment of cyanide effluents by oxidation and adsorption in batch and column studies. **Journal of Hazardous Materials, 166**(2–3), 1362–1366.

Zhang, W., Liu, W., Lv, Y., Li, B., & Ying, W. (2010). Enhanced carbon adsorption treatment for removing cyanide from coking plant effluent. **Journal of Hazardous Materials, 184**(1-3), 135–140.