CHAPTER II
LITERATURE REVIEW

This research will study the effect of nano zero-vaent ion coated on diatomite (nZVI-D) adsorbed lead, arsenic and cyanide, respectively under a batch reactor. The first, researcher will explain the physical and biological properties of lead, arsenic and cyanide, respectively. The second, researcher will give some information on the adsorption process, kinetics adsorption isotherm model and adsorption isotherm model. The third, researcher describes a mechanism of adsorption which is expected to occur.

2.1 Heavy metals and cyanide

In the current, the mining industry releases toxic chemicals into environmental, such as cyanide, arsenic, lead, mercury, and chromium. In addition, arsenic, lead and cyanide are extremely toxic. Heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. Whereas cyanide poisoning can occur through inhalation, ingestion and skin contact. One teaspoon of a 2% solution can kill a person.

2.1.1 Lead

Properties of lead

Lead is a transition metallic element which is face-centered cubic, with the lead–lead distance being 349 pm. It has the atomic number 82, Atomic mass is 207.2 g/mol, Electronegativity according to Pauling is 1.8, Vander waals radius is 0.154 nm and Isotopes is 13 as well as Density, Melting point and Boiling point of lead are 11.34 g/cm^3, 327°C, 1,755°C, respectively. Lead is a bluish-white lustrous metal. It is very soft, highly malleable, and a poor conductor of electricity. It is very resistant to corrosion but tarnishes upon disclosure to air. The Pb^{2+} species have relative with pH values in solution, this is Pb^{2+} present in the forms of Pb^{2+}, $Pb(OH)^+$, $Pb(OH)_2$ and $Pb(OH)_3^-$ at various pH values (Sheng et al., 2009) shown in Fig 2.1. At pH< 7.0, the main specie is Pb^{2+} and the predominant species at pH 7.0-10.0 are $Pb(OH)^+$ and $Pb(OH)_2$. The main species at pH > 10.0 are $Pb(OH)_2$ and $Pb(OH)_3^-$.

Toxicology of lead

Lead is one of the toxic heavy metals when adsorbed into the body. Lead is released into the surface water and groundwater from various industrial activities such as metal plating, oil refining and battery manufacturing, wood production and also combustion of fossil fuel, forest fires, mining activity and sewage wastewater, etc. (Ozdes et al., 2009). In fact, Lead is non-biodegradable and accumulate in a body which it enter the human body through inhalation, ingestion or skin contact. As a result, it can act as an accumulative toxic. Moreover, lead collects regularly in bones, brain, kidney and muscles and may cause many serious disorders like anemia, kidney diseases, nervous disorder and sickness even death (Kazi et al., 2008).

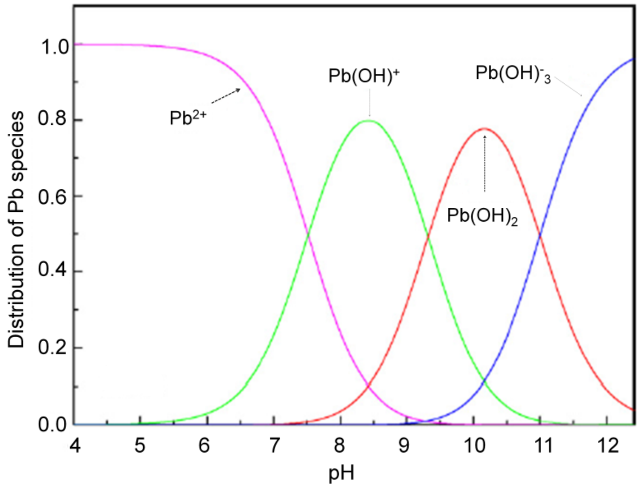

Figure 2.1 Distribution of Pb^{2+} species as a function of pH based on the equilibrium constants (Sheng et al., 2009)

2.1.2 Arsenic

Properties of arsenic

In natural environment, arsenic is hardly found as a free element. It can occur as the semi-metallic element (As), arsenate (As^{5+}), arsenite (As^{3+}), monomethylarsonate (MMAA), and dimethylarsinate (DMAA). The amount of each of these species depends on the redox conditions and the nature of anthropogenic input and biological activity. However, the organic arsenic (methanearsonic acid, cacodylic acid, methyldihydroxy arsine) not major significance in drinking water treatment. In contrast, the inorganic arsenic (As^{5+}) and arsenite (As^{3+}) are most widespread in drinking water. It has been found that As^{3+} is more transportable than As^{5+} due to its weaker attraction to soils and sediments (Zhao, Jia, Xu, & Zhao, 2011). In addition the As^{3+} species are more toxic than the As(V) (Jeon, Baek, Park, Oh, & Lee, 2009). Therefore, the toxicity of arsenic in water depends on the form, type of compound, and concentration in water.

As^{3+} is found primarily as H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-} under reducing environment (Chowdhury, Yanful, & Pratt, 2010) whereas different species of As^{5+}, namely H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}, under oxidizing environment (Salameh, Al-Lagtah, Ahmad, Allen, & Walker, 2010). Furthermore, oxidation-reduction potential (Eh) and pH are the most important parameters controlling arsenic species. The relationship between Eh, pH and arsenic species are illustrated in Fig. 2.2.

Toxicology of arsenic

Arsenic is one of the most toxic and non-degradable contaminants in aquatic systems. Arsenic has been contaminated into surface water and groundwater by human activities such as mining wastes, petroleum refining, sewage sludge, agricultural chemicals, ceramic manufacturing industries, geochemical reactions, industrial waste, fertilizers, and mining/smelting operations (Chowdhury et al., 2010; Mosaferi, Nemati, Khataee, Nasseri, & Hashemi, 2014). The World Health Organization (WHO) guideline value for arsenic in drinking water is 10 µg/L ("WHO | Guidelines for drinking-water quality - Volume 1," n.d.). The humans has been ingested a large amount arsenic and accumulated a long time which may cause the health problems. Arsenic cause diseases such as black foot disease, skin, lung and bladder cancers, anemia, diabetes, and disorders of the immune nervous and reproductive systems (Luther, Borgfeld, Kim, & Parsons, 2012). Additionally, the USEPA identify arsenic as a carcinogen.

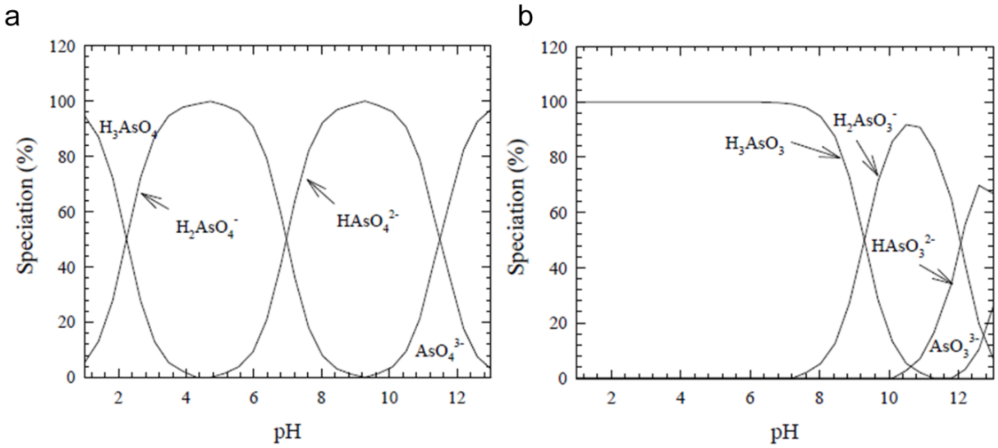

Figure 2.2 Distribution of (a) arsenate and (b) arsenite species as a function of pH based on the equilibrium constants (Chowdhury et al., 2010; Salameh et al., 2010)

2.1.3 Cyanide

Properties of cyanide

Cyanide is any chemical compound containing monovalent combining group CN. This group, known as the cyano group, involves a carbon atom triple-bonded to a nitrogen atom. In inorganic cyanides, such as sodium cyanide which are considered as salts of hydrocyanic acid, are highly toxic. The cyanide is isoelectronic with carbon monoxide and molecular nitrogen. Organic cyanides are usually called nitriles and the CN group is linked by a covalent bond to a carbon-containing group, such as methyl (CH_3) in methyl cyanide (acetonitrile). Inorganic cyanides are the most toxic than organic cyanides. In nature is found hydrogen cyanide more over than 99% shown in Fig.2.3. However, hydrogen cyanide is soluble but when the temperature and salinity increased as a resulted the solubility less. Wastewaters were contained with free and metal-complexes cyanides created from electroplating, extraction of gold and silver, metal cleaning, jewelry making, coke plant, plastic and chemical industries (Gupta, Balomajumder, & Agarwal, 2012).

Toxicology of cyanide

Free cyanide has been known as the most toxic species because of hydrogen cyanide, when human and aquatic organisms received cyanide in short or long-term exposure causing effect of serious respiratory and neurological (Do, Jo, Park, & Kong, 2012). Due to their toxic effects, US-health service cites 0.01 mg/L as guideline and 0.2 mg/L as allowable limit for cyanide in discharge (WHO, n.d.)

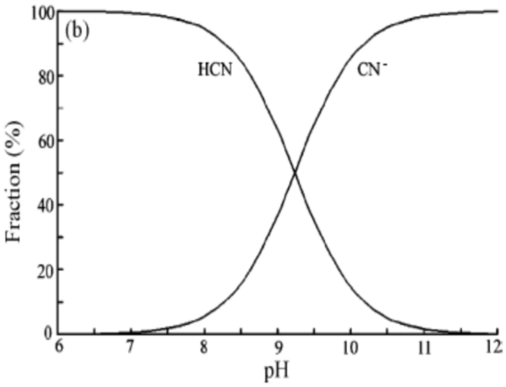

Figure 2.3 Distribution of cyanide species as a function of pH based on the equilibrium constants (Dash, Balomajumder, & Kumar, 2009)

The information above, they has been understood lead, arsenic and cyanide are extremely dangerous to organisms and human body. Therefore, the researcher has been studied the ways to treat lead, arsenic and cyanide in surface water and underground water. Certainly, there are many methods.

2.2 Treatment technologies

Methods has been used to remove lead, arsenic and cyanide from wastewater mainly precipitation (Chen, Luo, Hills, Xue, & Tyrer, 2009), flocculation (Han, Runnells, Zimbron, & Wickramasinghe, 2002), ion-exchange (Mondal, Balomajumder, & Mohanty, 2007), reverse osmosis, filtration (Bessbousse, Rhlalou, Verchère, & Lebrun, 2008; Leupin & Hug, 2005) and adsorption (Gupta, Saini, & Jain, 2005; Pan, Chiou, & Lin, 2010; Wang et al., 2014; Zhang, Lin, Chen, Megharaj, & Naidu, 2011). The precipitation is widely used to remove due to its simplicity of use but it must be improved sedimentation of sludge before discharge to environmental and unsuitable for household applications. Then, the flocculation process has been used chemicals in the system, cause of toxic sludge. Next, the ion-exchange and reverse osmosis are expensive technology and the systems need to take care. Whereas, the filtration process is high capability, but the system requires a lot of water and prepare wastewater before entering the system. To sum up, most of these methods are only suitable for the removal of heavy metal in low concentrations and often require extensive processing and high cost. Therefore, in this study has focused on removal of lead, arsenic and cyanide through adsorption because the system is able to removal from contaminated water in high concentrations, simple to operate and cost-effective.

2.3 Adsorption process

An adsorption is a process when a gas or liquid solute accumulates on the surface of a solid or a liquid at an interface or in an interfacial layer. Adsorption is effective in most natural physical, biological, and chemical systems. It is widely used in industrial applications such as synthetic resins and treated wastewater. The adsorption of solution can adhere to the surface only through Van der Waals (weak intermolecular). This is interactions between adsorbate molecules and the atoms of adsorbent (physical adsorption). In the same time, it occurs a monolayer resulting adheres to a surface through the formation of a chemical bond and electrostatic interactions (chemical adsorption). Thus, the adsorption depend on type of material which the adsorbent must have a large specific surface area and molecule of adsorbate with adsorbent.

2.4 Nano scale zero valent iron (nZVI) and support

In recent years, nano scale zero valent iron (nZVI) has been extensively acknowledged for its potential application for the treatment of contaminated water. It has high surface energy and reaction activity due to its large specific surface area. The physicochemical properties of nZVI and its reductive capacity allow its application in the rapid decontamination of many aqueous pollutants. The nZVI is produced by reduction of Fe^{2+}/Fe^{3+} become nZVI (Fe^0) which reducing with sodium borohydride ($NaBH_4$) shown in Eq. 2.1-2.2.

$$2Fe^{2+} + BH_4^- + 2H_2O \rightarrow 2Fe^0 + BO_2^- + 2H_2 + 4H^+ \quad (2.1)$$

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow Fe^0 + 3B(OH)_3 + 6H_2 + 9H^+ \quad (2.2)$$

nZVI has a relatively low standard potential allowing it to efficiently donate electrons to pollutants, converting them into their reduced forms. In the process, Fe is transformed from Fe^0 to Fe^{2+} as expressed in following equation:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \qquad E_{0cell}\, Fe^{2+}/Fe^0 = -0.440V \quad (2.3)$$

Therefore, theoretically Fe^0 can reduce any pollutant that has a higher reduction potential than −0.440 V. Additionally nZVI has a good dispersive properties and is able to absorb pollutants in aqueous suspensions. So, nZVI can remove contaminants through reduction or adsorption methods. For example, arsenic was reduced with nZVI in first step, and then it was adsorbed into iron oxides and hydroxides formed during oxidation (Kanel, Manning, Charlet, & Choi, 2005; Manning, Hunt, Amrhein, & Yarmoff, 2002; Yan, Ramos, Koel, & Zhang, 2012). Whereas, nZVI can be completely and quickly oxidize As^{3+} to As^{5+}. As^{5+} is removed by adsorption on newly formed hydrous ferric oxides. However, As^{3+} can be oxidized to As^{5+} in the nZVI system, but As^{5+} was inefficiently removed and it still partly remains in aqueous solution as potential pollutants and need further removal (Keenan, & Sedlak, 2008; Du et al., 2013). Thus, it is necessary to remove the As^{5+} during oxidation by adsorption method. In addition, nZVI usually appears powders and not applied in fixed-bed columns or flow-through systems due to the high pressure drop. Next, nZVI can agglomerate due to Van der Waals and magnetic attraction forces which may lead to the benefits loss. Hence, it is necessary to load nZVI onto supporting materials as can improve the adsorption capacity with reduce the aggregation of nanoparticles for the treatment of arsenic-contaminated drinking water. For example, Zhang et al. (Zhang, Li Y., Li J., Hu, & Zheng, 2011) prepared nZVI with pillared clay for removal of nitrate. Liu et al. (Liu, Wang, Zhao, & Yang, 2012) used chitosan-nZVI adsorption hexavalent chromium from wastewater and Seol et al. (Kim et al., 2013) prepared zeolite-nZVI removal Pb^{2+}. In this study, a diatomite ($SiO_2.nH_2O$) was used to the support. The diatomite is a kind of natural zeolite, lightweight, high porosity

(80-90% voids), high surface area and chemical inertness. Thus, it becomes an interesting material to use as a support for nZVI.

2.5 Effect adsorption

2.5.1 Effect of adsorbent dose

The effect of adsorbent dose has been involved the removal efficiency of pollution. The removal of metal ions increases sharply with increase in adsorbent dosage due to the availability of more binding sites on the adsorbent dosage surface. It can be explained that the adsorbent dose increased lead to increases in active sites on the surface of adsorbent (Mondal, Majumder, & Mohanty, 2008) and easier infiltrated of a metal ion to the active site (Sarı, Tuzen, Cıtak, & Soylak, 2007). In contrast, adsorbent dosage excess cause adsorption efficiency constant or decreased which may be due to the reduction in concentration gradient and also due to overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area. For example, the percent adsorption of As^{3+} with nZVI on activated carbon (nZVI/AC) increased 40% with increasing adsorbent load from 0.1 g/L to 3.0 g/L. Moreover, the nZVI/AC can treat As^{5+} more than 99 % (Zhu, Jia, Wu, & Wang, 2009). The study of Mohammad et al. found that percentage removal of arsenite and arsenate increased from 44% and 60%, respectively to more than 95% when the dose of S-nZVI applied increased from 0.1 to 1 g/L (Mosaferi et al., 2014).

2.5.2 Effect of initial concentration of solution

The solution initial concentration is considered as one of the most important factors affecting the removal process of heavy metal contaminants. The percentage removal of Pb^{2+} was decreased from 97.6% to 22.5% when the initial concentration increased from 30 to 1,000 mg/L of S-NaOH-NZVI (Arshadi, Soleymanzadeh, Salvacion, & SalimiVahid, 2014).

Moreover, the removal of Hg^{2+} and Cr^{6+} was decrease with increase of initial concentrations (Liu, Wang, Yan, & Zhang, 2014) similar to the other research (Kim et al., 2013; Rahmani, Ghaffari, & Samadi, 2011). However, the heavy metal concentrations increased result that the adsorption capacities raised due to the interaction between the heavy metal and adsorbent. It provides the vital driving force to defeat the resistances to the mass transfer of heavy metal between the aqueous and adsorbent. The observed improvement of heavy metal uptake with increase in the initial metal ion concentration will be due to an increase in electrostatic interactions (Arshadi et al., 2014). In the other hand, the research of Mandal, et al. (n.d.) found that an increase of As^{3+} initial concentration lead to the increase percentage removal, due to the fact that at higher adsorbate concentration, the free sites available approaches saturation. Because, the removal method can be implemented remove As^{3+} from water present in any concentration.

2.5.3 Effect of temperature

Temperature is an important factor of adsorption. The increase and decrease of temperature generate the exothermic and exothermic of cations and anions for an adsorbent surface, respectively. For instance, Seol Ah Kim, et al. found that temperature did not significantly affect adsorption capacity, and suggest that adsorption takes place by chemical bonds between Pb^{2+} and Z-nZVI which ranged from 99.8% at 60ºC to 94.6% at 5ºC (Kim et al., 2013). As, Z. Chen et al. reported that when changing the temperature from 25ºC up to 40ºC during the decoloration of crystal violet (CV) from water, the decoloration capacity of K–nZVI does not change significantly (Chen et al., 2013). Therefore, the processes have dissociation of solution, more rapid diffusion into the internal pores of the composite particles and the formation of a reactive surface complex or the activation energy increased as the temperature increase (Chen et al., 2013; Kim et al., 2013).

2.5.4 Effect of initial pH

The pH value of the solution plays an important role in the adsorption of heavy metal on adsorbent and influences the dissociation of ions in solution and the surface of the adsorbent. The arsenic adsorption onto the surface nZVI was proposed include transplantation to the surface, dissociation or deprotonation of arsenic solution and surface complexation. The adsorption reaction was mainly controlled by electrostatic attraction or repulsion of the aqueous arsenic species with the surface of the adsorbent. Additionally, a pH of zero point charge (pH_{ZPC}) of the adsorbent is factor which controls the speciation of aqueous. It is well known that solid surface is positively charged at pH of solution below pH_{ZPC} causing in increased electrostatic attraction and negatively charged at pH of solution above pH_{ZPC} resulting electrostatic repulsion with anionic arsenic species, thus leading to more or less arsenic adsorption.

For example, the removal efficiency of As^{5+} was about 100 % at pH 6-7, while pH 8, the removal efficiency is reduced to 61%. As a result, the predominate As^{5+} species in aqueous solution is $H_2AsO_4^{-}$ in the range of pH 2 to 6 which the adsorbent surface display positive ion at pH solution below pH_{zpc}. The adsorption was occurred by the reaction and electrostatics attraction force between ions of As^{5+} and the surface of nZVI-D leading to the formation of surface complexes. Contrary, solution above pH 6 adsorption of As^{5+} decreases because of pH of solution more than pH_{pzc} and competition between $HAsO_4^{2-}/AsO_4^{3-}$ and OH^{-} ions for active sits on nZVI-D. Therefore the arsenate adsorption decreased significantly all the way with increasing pH which this has been well documented in previous works of As^{5+} adsorption.

2.5.5 Effect of contact time

It is observed that the uptake of the heavy metal increases with time. The amount of Pb^{2+} adsorbed increased by FTAW and STAW with increase in contact time and reached equilibrium after 150 min (Örnek, Özacar, & Şengil, 2007). As well as a nZVI-Lab and nZVI/DE-C removed simazine was more rapidly within 5 min and slowly reached the maximum within 30 min (Sun, Zheng, Ayoko, Frost, & Xi, 2013). Because the diffusion of Pb^{2+} ions through the solution to the surface of adsorbents is affected by the lead concentration, since agitation speed is constant. An increase of the lead concentration accelerates the diffusion of Pb^{2+} from the lead solution onto adsorbents due to the increase in the driving force of the concentration gradient.

2.6 Equilibrium adsorption models

The adsorption isotherms refer to molecules of solution which are absorbed on the adsorbent at equilibrium as a function of initial concentration, which it is importance in the design of adsorption system (Momčilović, Purenović, Bojić, Zarubica, & Ranđelović, 2011).

The Langmuir adsorption model is assumed that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface (Hameed, Mahmoud, & Ahmad, 2008). The expression of the Langmuir model is given by Eq. (2.3):

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

where K_L is the Langmuir adsorption constant (L/mg), q_e is the amount of adsorption equilibrium (mg/g), q_m is the monolayer adsorption capacity of the adsorbent (mg/g) and C_e is the solute concentration at equilibrium (mg/L).

The Langmuir isotherms can be depicted in terms of a dimensionless factor or equilibrium parameter, R_L (dimensionless separation factor) was given by Eq. (2.4):

$$R_L = \frac{1}{1 + K_L C_0} \tag{2.4}$$

where, C_o is initial concentration of arsenate solution (mg/L) and R_L value indicates the adsorption nature to be either unfavourable if R_L >1, linear if R_L =1, favourable if 0< R_L <1 and irreversible if R_L =0 (Karagöz, Tay, Ucar, & Erdem, 2008; Senthil Kumar, 2014).

The Freundlich adsorption model is based on heterogeneous surfaces and multilayer sorption (Ho, & McKay, 1998). Linear form of Freundlich equation is shown as Eq. (2.5):

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

where K_F is Freundlich adsorption constant (L/g) and n is n are Freundlich constants, involved to adsorption capacity, and n is an indication of how favorable the adsorption process. The value of n > 1 represents favorable adsorption condition (Hameed, Salman, & Ahmad, 2009). This is the change in adsorbed concentration is greater than the change in the solute concentration (Ng, Losso, Marshall, & Rao, 2002).

The Dubinin–Radushkevich (D–R) adsorption isotherm model predicts the energy of adsorption per unit of adsorbate and a maximum adsorption capacity for the adsorbent. A linear form of Dubinin-Radushkevich isotherm is (Sari, Tuzen, Citak, & Soylak, 2007):

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

where q_d is the Dubinin-Radushkevich monolayer capacity (mg/g), β is a constant related to adsorption energy, and ε is the Polanyi potential which is associated to the equilibrium concentration as follows:

$$\varepsilon = \frac{RT}{M}\ln\left(1+\frac{1}{C_e}\right) \tag{2.7}$$

where R is the gas constant (8.314 J/mol·K), M is the molecular weight of the adsorbed, T is the absolute temperature and C_e is the solute concentration at equilibrium (mg/L), The mean adsorption energy, E (kJ/mol) is as follows:

$$E = \frac{1}{\sqrt{2\beta}} \tag{2.8}$$

The adsorption energy presents information with regard to physical and chemical characteristics of adsorption. The magnitude of E is between 8-16 kJ/mol, the adsorption process follows chemical ion-exchange, while for the values of $E < 8$ kJ/mol, the adsorption process is the physical adsorption (Caliskan, Kul, Alkan, Sogut, & Alacabey, 2011)

2.7 Kinetic adsorption isotherms

The reaction mechanism is able to be obtained from the adsorption kinetic isotherms and adsorption isotherms, kinetic adsorption isotherms study can be extremely beneficial to determine the information about the mechanism of adsorption and the efficiency of the adsorbents for the removal of heavy metal. The First, the kinetics of adsorption was analyzed by the pseudo-first-order kinetic model (Mishra & Patel, 2009) which could be shown by the following equation:

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

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

The second, the pseudo-second-order rate expression has been applied for analyzing the chemisorption kinetics from liquid solutions is linearly expressed as:

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

The pseudo-second-order rate constants were determined experimentally by plotting t/q against t , where q_e and q_t are the amounts of solute adsorbed (mg/g) at equilibrium and time (t), respectively; and k_2 is the rate constant of pseudo-second-order adsorption (g/mg·min). The initial adsorption rate, h (mg/g·min), as t_0 can be defined as:

$$h = k_2 q_e^2 \tag{2.11}$$

Finally, the different concentrations of adsorption with time could be used to appraise the function of diffusion in the adsorption process. The intra-particle diffusion rate was given by the equation:

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

where k_i is the intra-particle diffusion rate constant (mmol/g·min$^{1/2}$). The rate of absorption depends on the size of adsorbate molecule or ion, the porous nature of adsorbent, the concentration of the adsorbate and the pore-size distribution of the adsorbent, and degree of mixing (Özacar, Şengil, & Türkmenler, 2008). The adsorption process is considered to comprise three steps, one of which can be the rate-controlling step: (i) mass transfer across the external boundary layer film of liquid surrounding the outside of the particle; (ii) adsorption at a site on the surface and the energy depend on the binding process, this step is often assumed to be rapid; (iii) diffusion of the adsorbate molecules to an adsorption site either by a pore diffusion process through the liquid filled pores or by a solid surface diffusion mechanism. Since the adsorption step is very rapid, it is assumed that it does not influence the overall kinetics. Therefore, the adsorption will be controlled by either surface diffusion or intra-particle diffusion. According to this model, a plot of q_t versus $t^{1/2}$ should be linear when the adsorption process is involved in the intra-particle diffusion. If the plot passes through the origin, the intra-particle diffusion may totally be the rate-controlling step. If it does not pass through the origin, the boundary-layer diffusion controls the adsorption to some degree and the intra-particle diffusion is not the rate-controlling step totally, but the other processes may control the rate of adsorption (Boparai, Joseph, & O'Carroll, 2011).

2.8 Thermodynamic studies

Thermodynamic parameters including Gibbs free energy change (ΔG^{o}), enthalpy change (ΔH^{o}) and entropy change (ΔS^{o}) for the adsorption process were obtained from the experiments carried out at the different temperatures using the following equations (Boparai et al., 2011; Sari et al., 2007):

$$\Delta G^{0} = -RT \ln K_L \tag{2.13}$$

where R is the universal gas constant (8.314 J/mol·K), T is the temperature (K) and K_L value was calculated using the following equations:

$$K_L = \frac{q_e}{C_e} \tag{2.14}$$

where q_e and C_e are the equilibrium concentrations (mg/g) and in the solution (mg/L), respectively.

The enthalpy change (ΔH^0) and entropy change (ΔS^0) of the adsorption were estimated from the following equation:

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{2.15}$$

The values of these were calculated from the slope and t of the intercept of the plot of $ln\ K_L$ versus $1/T$. The enthalpy (ΔH^0) and entropy (ΔS^0) can be obtained from the slope and intercept of a Van't Hoff equation of (ΔG^0) versus:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{2.16}$$

where ΔG^0 is the Gibbs free energy change (J), R the universal gas constant (8.314 J/mol·K) and T is the absolute temperature (K).

2.9 The mechanisms of lead, arsenic and cyanide removal by nZVI-D

The step of nZVI-D removed solution. Firstly, nZVI are reduced by water and oxygen which produces ferrous iron shown in Eq. 2.17-2.19.

Anaerobic corrosion: $Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$ (2.17)

$2Fe^0 + 4H^+ + O_2 \rightarrow 2Fe^{2+} + 2H_2O$ (2.18)

Aerobic corrosion : $2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^-$ (2.19)

The equations above, the Fe^{2+} react with H_2O/O_2 or OH^- producing Magnetite (Fe_3O_4), Ferrous hydroxide ($Fe(OH)_2$) or Ferric hydroxide ($Fe(OH)_3$) depending on the redox and pH of the system displayed in Eq. 2.10-2.13.

$$6Fe^{2+} + O_2 + 6H_2O \rightarrow 2Fe_3O_4 + 12H^+ \tag{2.10}$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \tag{2.11}$$

$$6Fe(OH)_2 + O_2 \rightarrow 2Fe_3O_4 + 6H_2O \tag{2.12}$$

$$Fe_3O_4 + O_2 + 18H_2O \rightleftharpoons 12Fe(OH)_3 \tag{2.13}$$

2.9.1 The mechanisms of lead

The standard reduction potential of Pb^{2+}/Pb^0 is -0.1263 V which has more positive than Fe^{2+}/Fe^0 (-0.4402 V), therefore Pb^{2+} can be reduced to Pb^0 in solution electrochemically. Moreover, The Fe_2O_3, FeOH and FeOOH can react with the Pb^{2+} produced FeOPbOH, PbO-Fe, PbO_2-Fe_2O_3 and PbO-FeOOH. In addition, the Pb^{2+} in aqueous solution is absorbed on the surface of diatomite (SiO_2 and Al_2O_3). The mechanism was suggested by Fig. 2.4

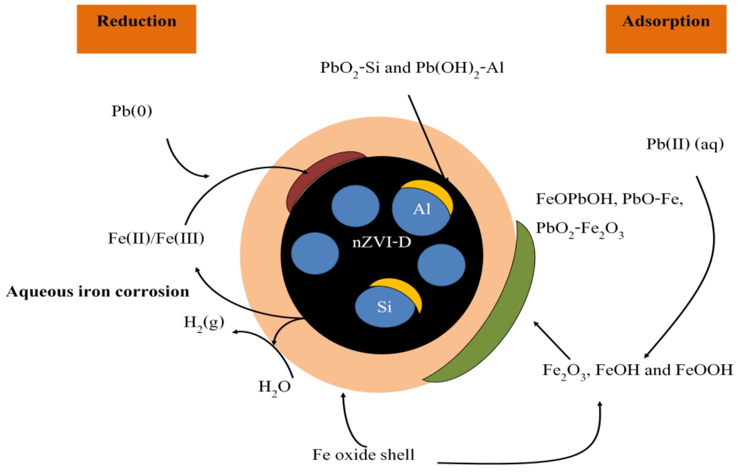

Figure 2.4 The mechanism of adsorption Pb^{2+} from aqueous solution by nZVI-D

2.9.2 The mechanisms of arsenic adsorption

Arsenic adsorption mechanism of zero valent iron nanoparticles coated diatomite (nZVI-D) was expected to four steps. The first step, the oxidation of As^{3+} was produced As^{5+} using nZVI-D as a catalyst. Next, the As^{5+}/As^{3+} were reduced to As^0 by electrons produced from Fe^0 oxidations and diffused to near the oxide/Fe^0 interface explained by Eq. 2.14.

$$Fe^0 + As^{5+}/As^{3+} + H_2O/O_2 \rightarrow Fe^{2+}/Fe^{3+} + As(0) + H_2 \tag{2.14}$$

Then, the ions were attracted between As(V)/As(III) and ferrous/ferric oxides surface sites. Next iron arsenic was precipitated on the surface of adsorbents proposed by Eq. 2.15.

$$Fe^{2+}/Fe^{3+} + As^{5+}/As^{3+} \rightarrow Fe \equiv As^{5+}/As^{3+} + H_2O \tag{2.15}$$

The arsenic ions diffused into the oxide surface by solid-phase redox transformation mechanism. Arsenic preferred to accumulate at the surface of nZVI-D forming a thin layer of Fe-As intermetallic. Finally, the existence of diatomite enhanced arsenic adsorption which the formation appeared As-Al and As-Si bond. Some arsenic ions might be transferred to the surface of diatomite and then arsenic was precipitated on adsorbent surface. Thus, Al and Si in diatomite structures played a significant role in enhanced reactivity and stability of nZVI. The mechanism was proposed by Fig. 2.5.

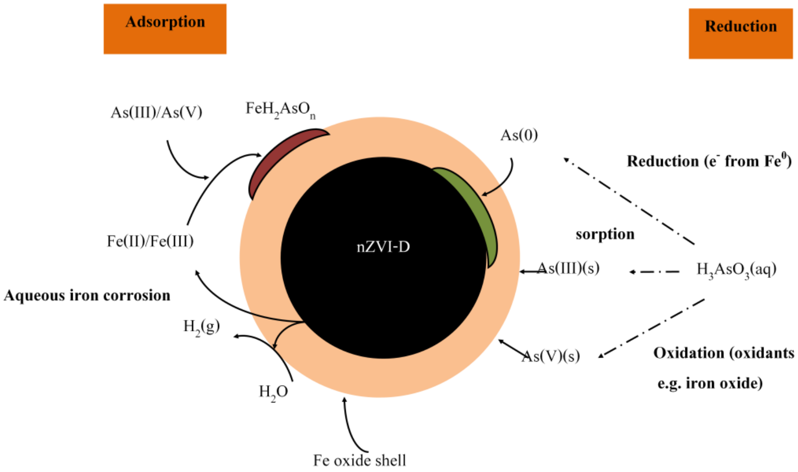

Figure 2.5 The mechanism of adsorption arsenic from aqueous solution by nZVI-D

2.9.3 The mechanisms of cyanide

Free cyanide are adsorbed by nZVI-D which has the mechanism to absorb, namely, iron oxide was protonation or deprotanation with hydrogen ions which the positive or negative ions of iron oxide reacted with CN^- and HCN.

$$Fe_s\text{- }OH + H^+ \rightleftharpoons Fe_s\text{- }OH_2^+ \tag{2.16}$$

$$Fe_s\text{- }OH \rightleftharpoons H^+ + Fe_s\text{- }O^- \tag{2.17}$$

Thus, iron oxide ions are attracted to the CN^- and HCN Eq. 2.18-2.19.

$$Fe_s\text{–}OH^{+2} + CN^- \rightleftharpoons Fe_s\text{–}OH^{+2} \cdots CN^- \tag{2.18}$$

$$Fe_s\text{–}OH + HCN \rightleftharpoons Fe_s\text{–}CN + H_2O \tag{2.19}$$

In sum up, the attraction between iron oxide which is positively charged and free cyanide which it is negatively charged. Thus, cyanide is precipitated and adsorbed on the nZVI-D during the process. That is the oxidation reaction of cyanide into cyanate (CNO^-) with low toxicity. Fig. 2.6 showed the mechanism of adsorption free cyanide.

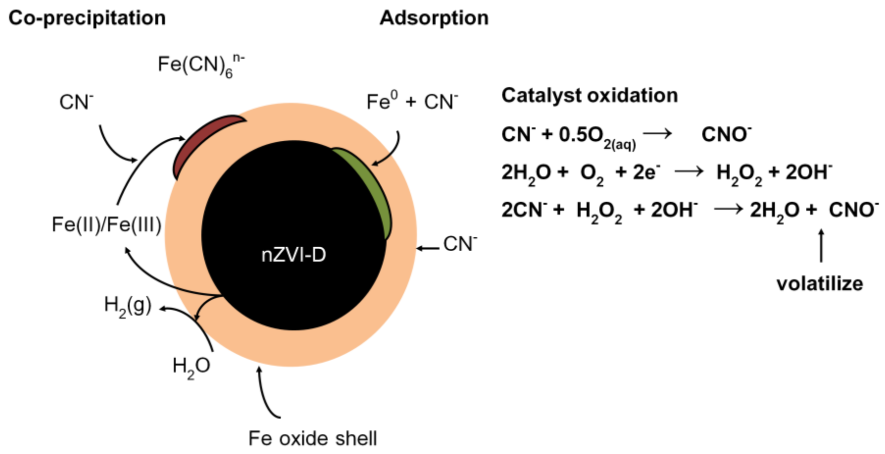

Figure 2.6 The mechanism of adsorption free cyanide from aqueous solution by nZVI-D

2.10 Response surface methods

Response Surface Methods (RSM) are designs and models for working with continuous treatments when exploring for optimum operating conditions through experimental methods. The application of RSM to design optimization is targeted at reducing the cost of expensive analysis methods and fewer experimental runs to generate the information necessary (Fermoso et al., 2010). Therefore the RSM used to design optimization applications and useful statistical technique which has been applied in research in complex variable processes. This technique involves the design of experiments and multiple regression analysis as tools to assess the effects of two or more independent variables on dependent variables. RSM helps researchers to build models, evaluate the effects of several factors and establish the optimum conditions for the desired responses (Fermoso et al., 2010; Jeong, Yang, & Park, 2009). The analysis of variance (ANOVA) provides statistical results upon which analyze experiments can be used to enable researchers to evaluate the suitability of the models (Ghafari, Aziz, Isa, & Zinatizadeh, 2009).

The research studies generally used different technique for process optimization. The central composite design (CCD) was used to find optimization in this study. This is, the study must be required small number of the completed experiments of the treatment wastewater for modeling process. The optimum condition for the adsorption of heavy metal was conducted based on a CCD and analyzed using RSM. The effects of the process were investigated at five different levels in the CCD: negative star, minimum, center, maximum and positive star points coded as −α,−1, 0, +1 and +α, respectively (Fig. 2.7).

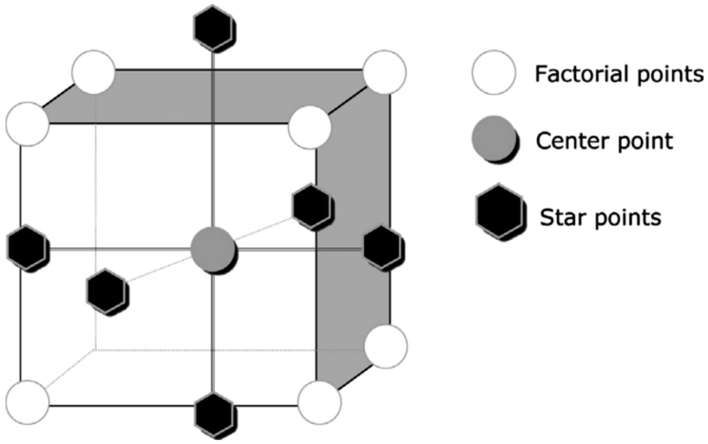

Figure 2.7 A modified figure of central composite design for three factors (Onal, & Frigi, 2014)

The percentage heavy metal removal heavy metal 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 heavy metal (mg/L) and C_t is the concentration of heavy metal (mg/L) after adsorption at time. Y is the percentage of removal heavy metal.

The experimental results of CCD were fitted by the response surface regression procedure, using the following quadratic equation that is given as:

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i=1}^{k} b_{ij} X_i X_j \tag{2.21}$$

where Y is a response variable of the percentage removal of heavy metal. The b_i is the regression coefficient for linear effects; b_{ii} is the regression coefficient for squared effects; b_{ik} is the regression coefficient for interaction effects, and x_i is the coded experimental level of the variables.

A minitab, a statistical software package, was used for analysing regression equation of the experimental data and also to plot a response surface graphs. The statistical significance and the model terms were evaluated via the Fisher's test. To evaluate a quality of fitting equation, a coefficient of determination (R^2) and an adjusted R^2 were used. Moreover, the response surface and contour plots of the model-predicted responses were utilized to assess an interactive relationships between significant variables.

The adjusted R^2 is a modified version of R^2 that has been adjusted for the number of predictors in the model. The adjusted R-squared increases only if the new term improves the model more than would be expected by chance. It decreases when a predictor improves the model by less than expected by chance. It is always lower than the R-squared. In addition, R^2 assumes that every single variable explains the variation in the dependent variable, while the adjusted R^2 tells you the percentage of variation explained by only the independent variables that actually affect the dependent variable. The R^2 value is high, close to 1, which is desirable. The predicted R^2 is in reasonable agreement with the adjusted R^2. The adjusted R^2 value is particularly useful when comparing models with different number of terms. This comparison is however done in the background when model reduction is taking place. Adequate precision compares the range of the predicted values at the design points to the average prediction error. Furthermore, the lack of fit is not significant for the precipitation model ($p > 0.05$). This means that there is only > 5% chance that a lack of fit could occur due to noise. In the RSM design, insignificant values for the lack of fit factors combined with larger p-values usually exist to determine the significance of the model.

The diagnostic plots of the optimization study are shown in Fig. 2.8a-d. The standard residuals calculated from predicted and experimental results show well fit the model satisfies the assumptions of the analysis of variance (ANOVA). The results are possibly due to the presence of a normal probability plot that was plotted approximately along a straight line as shown in Fig 2.8a. The Fig. 2.8b shows the frequency of standard residuals shown in normal distributions. The Fig. 2.8c presents random scatter plot of standard residuals versus the fitted value presented as randomly scattered around the zero line. Fig. 2.8d exhibits the standard residuals versus observation order results, which should oscillate in a random pattern around the zero line. This is the results can conclude that all of experimental orders were not observed in significant error.

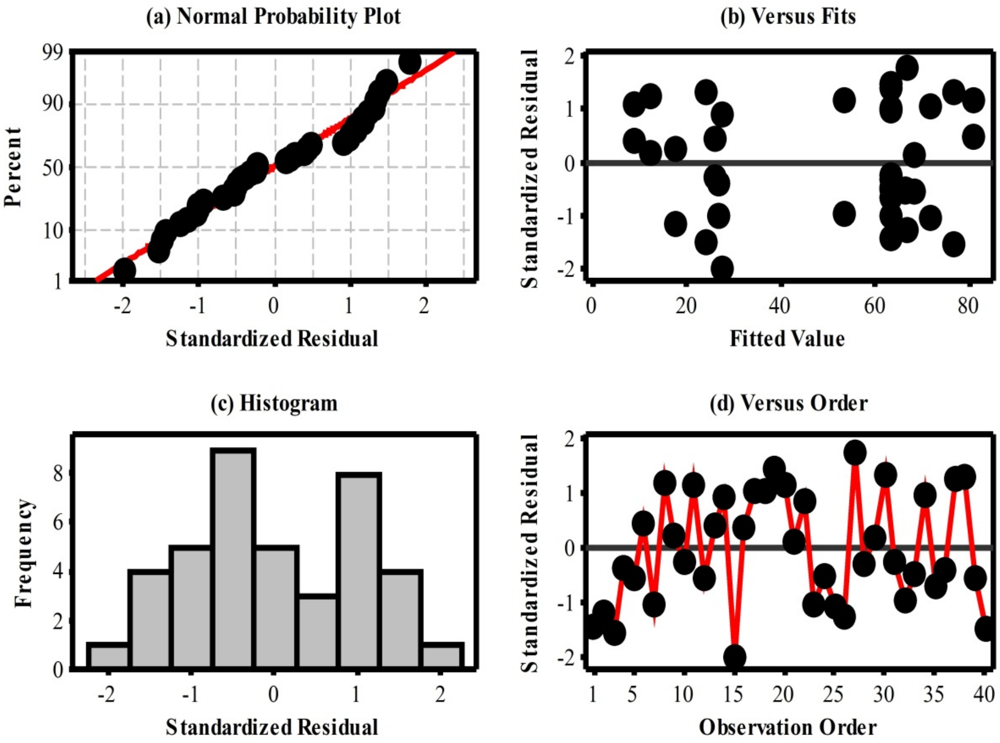

Figure 2.8 Internal standard residual plots versus normal probability, histogram, fits and order

When, the effect is more than one response therefore, it is important to look for the optimum condition which has the interaction between the effects of response. The objective understands the response changes which adjusted the effect variables. In general, the response surface can be shown in graph. The graph is helpful to see the shape of a response surface. Hence, the factor $f(X_1, X_2)$ can be plotted versus the levels of X_1 and X_2 as shown as Fig. 2.9.

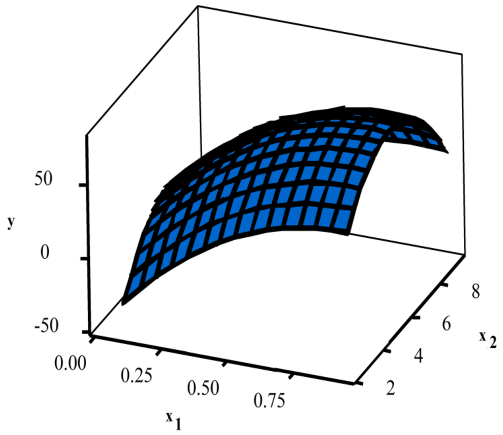

Figure 2.9 Response surface plots of response value (Y) versus variable effect (X_1 and X_2)

Fig. 2.9. Show each value of X_1 and X_2 predict Y-value. A three-dimensional graph displays the response surface from the side which called a response surface plot. Sometimes, it is less complicated to view the response surface in two-dimensional graphs. The contour plots can show contour lines of X_1 and X_2 pairs that have the same response value (Y). An example of contour plot is as shown in Fig. 2.10.

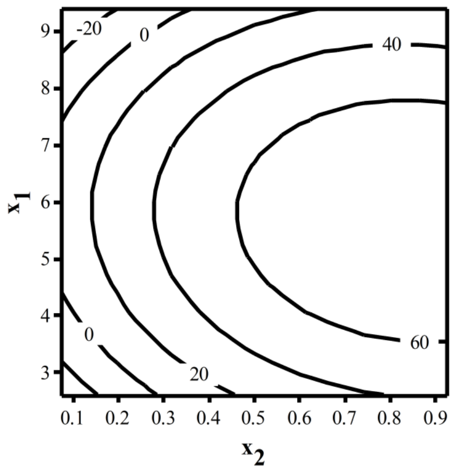

Figure 2.10 Contour plots of response value (Y) versus variable effect (X_1 and X_2)

2.11 List of abbreviations

Y	percentage heavy metal removal
C_e	equilibrium concentrations solution (mg/L)
C_o	initial solution concentrations (mg/L)
C_t	concentration solution at time (mg/L)
E	mean adsorption energy (kJ/mol)
k	number of factors studied and optimized in the experiment
k_1	rate constant of pseudo-first-order adsorption (min^{-1})
k_2	rate constant of pseudo-second-order adsorption (g/mg·min)
K_D	Dubinin-Radushkevich constant
K_F	Freundlich adsorption constant (L/g)
K_L	Langmuir adsorption constant (L/mg)
k_{i1}	intra-particle diffusion rate constant at slope 1 ($\text{mmol/g·min}^{1/2}$)
k_{i2}	intra-particle diffusion rate constant at slope 2 ($\text{mmol/g·min}^{1/2}$)
M	mass of adsorbent (g)
n	Freundlich constants
q_e	adsorption capacity at equilibrium (mg/g)
$q_{e.exp}$	adsorption capacity at equilibrium for experimental(mg/g)
$q_{e,cal}$	adsorption capacity at equilibrium for calculated (mg/g)
q_D	adsorption capacity at equilibrium for Dubinin-Radushkevich isotherm (mg/g)
R_L	dimensionless separation factor of Langmuir adsorption
q_{max}	adsorption capacity at equilibrium for Langmuir isotherm (mg/g)
q_t	adsorption capacity at time (mg/g)
R^2	determination coefficients
R^2_{adj}	adjusted determination coefficients
R^2_{pre}	predicted determination coefficients
SD	standard deviation
t	time (min)
V	volume of the solution (L)
Y	response denoted as the predicted $\text{As}^{5+/}\text{As}^{3+}$ percentage adsorption
X_i, X_j	coded values of variables