CHAPTER IX
CONCLUSIONS

Nano scale zero-valent iron supported on diatomite (nZVI-D_2) was synthesized by impregnating the surface of diatomite with ferric sulphate, followed by chemical reduction with $NaHB_4$. The XPS and FT-IR spectroscopy confirmed the formation of nZVI in the surface of diatomite. This is, the core of nZVI is consisted mainly of Fe^0 and the shell is largely of iron oxides/hydroxides origin formed from the oxidation of nZVI. The results of SEM and TEM indicating that diatomite prevented aggregation and help to well disperse of nZVI onto the surface.

The study performance of nZVI-D_2 used to remove lead, arsenic, and cyanide in the aqueous solution. In the cause of lead removal was found that nZVI-D_2can be used an effective adsorbent for the rapid removal of lead (100 mg/L) in 10 min. The equilibrium adsorption data were described by the Langmuir, the Freundlich and the D-R isotherm models. The maximum adsorption capacity of Pb^{2+} on nZVI-D_2 was 158.73 mg/g at the pH of 5. The D-R isotherm result indicated that the mean adsorption energy was shown 54.78 kJ/mol indicating that the adsorption of Pb^{2+} on nZVI-D was chemical adsorption. The pseudo-second-order kinetic model was well fitted for the adsorption of lead ions. The rate-controlling step of adsorption process was the film diffusion and intra-particle diffusion. The adsorption process of lead ions on nZVI-D was spontaneous and endothermic. For the mechanism of nZVI-D_2 to remove Pb^{2+}, it is proposed that lead ions in aqueous solution was adsorbed by nZVI-D_2 and reduced to Pb^0 by ZVI on diatomite.

Whereas, the result of As^{5+} removal by central composite design (CCD) was found that initial concentration effect of solution displayed a negative effect, while adsorbent dose and pH revealed positive effects on adsorption rate. The optimal condition of central composite design (CCD) at 1 min were 5.89 of initial pH, 0.8821 g/L of adsorbent dosage and initial 325 μg/L concentration which As(V) was removed up to 96.96%. The kinetic adsorption studies showed that the adsorption process well fit with pseudo-second-order kinetic model. In fact, the intra-particle diffusion model described that mass transfer and intra-particle diffusion were rate-limiting step. At the same time, the equilibrium adsorption data were well fit with Langmuir isotherm indicating that the adsorption caused monolayer adsorption onto homogeneous surface with a finite number of identical sites. The XANES and XRF results were shown the changing structure of nZVI by reaction time. The information suggested to the reaction of 4 pathway of As^{5+}- nZVI-D_2 adsorption. First pathway, the As^{5+} was reduced to As^0 and diffused to near the oxide/Fe^0 interface. Second and third pathway, $H_2AsO_4^-$ ions were attracted ferrous/ferric oxides forming FeH_2AsO_4 and As^{5+} accumulated at the surface of nZVI-D_2 forming a thin layer of FeOAsOOH, respectively. Next, the FeH_2AsO_4 and FeOAsOOH precipitated and collected on the oxide shell of adsorbents. Finally pathway, the $H_2AsO_4^-$ will be attracted bond with Al and Si on the surface of diatomite as $As(OH)_2$-Al, AsO_2-Si and AsO-Si, respectively.

In the cause of As^{3+}, the removal efficiency increased as the adsorbent dosage was raised. The ions of As^{3+}in the solution depending on the pH which involved the electrostatics interaction between the adsorbent and the adsorbate, this is, pH 2.6 was the best removal. Whereas, the percentage removal regularly decreased this was increasing initial concentration of As^{3+}. The maximum As^{3+} removal (>100 %) were nZVI-D dose 0.925 g/L, pH 2.6 and initial As(III) concentration 1,175 µg/L in the reaction time 1 min. The adsorption isotherms found that Langmuir isotherm ($R^2 > 0.995$) were well fit better than Freundlich ($R^2 > 0.929$) and Dubinin–Radushkevich ($R^2 > 0.978$) isotherm. It is clear that the adsorption involved the formation of a monolayer of As^{3+} particles coverage on a surface of nZVI-D_2. The adsorption capacity was 1,359 µg/g in 20 min. This is a fast uptake was an indicative that the active sites on nZVI-D were readily accessible for As^{3+} adsorption. The kinetic adsorption model well fit with pseudo-second-order kinetic more than pseudo first-order kinetic. The intraparticle diffusion was not rate controlling step. The removal mechanism can be concluded that As^{3+} was removed by a rapid chemical adsorption, precipitation and reduction on the nZVI-D_2. A mechanism for As^{3+} removal by nZVI-D_2 is proposed similar to As^{5+} but, the removal of As^{3+} increased the oxidation process became As^{5+} in the adsorbent.

Finally, the percentage removal of cyanide decreased when initial concentration increased while the percentage removal increased when reaction time increased. The adsorption isotherm models are well fitted with Langmuir isotherm more than Freundlich isotherm indicating that the adsorption cyanide with nZVI-D_2 describes monolayer adsorption. 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 kinetic adsorption isotherms follow by the pseudo second order rate and intra-particle diffusion. The cyanide was adsorbed by nZVI-D_2 which the chemical adsorption involving valence forces and the rate-limiting step were film diffusion and intra-particle diffusion.

In sum up, this work has demonstrated the potential application of nZVI-D_2 for the effective removal lead, arsenic, and cyanide from contaminated water as a rapid, easy and low cost method. The adsorption of lead, arsenic, and cyanide nZVI-D_2 was chemical adsorption.