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THESIS

OPTIMAL CONDITION FOR HEAVY METALS REMOVAL FROM WASTEWATER USING WATER TREATMENT SLUDGE/NANO ZERO VALENT IRON COMPOSITE

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A Thesis Submitted in Partial Fulfillment of
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Chromium and lead were concerned as toxicants contaminated in water resources because of the widely used for electroplating industries. For the remediation effectiveness enhancement, nano zero valent iron (nZVI) was modified with porous media. The optimal conditions of chromium and lead removal were studied by varying ratio of WTS/nZVI, and initial concentration and pH of chromium and lead solution in order to describe the adsorption isotherm and kinetics. The optimal ratio of water treatment sludge/nano zero valent iron (WTS/nZVI) composite was WTS/nZVI 1:1 weight by weight which can remove 10-80 mg/L hexavalent chromium (Cr(VI)) for 99% removal within 45 minutes–6 hours. The appropriate initial pH of Cr(VI) solution was pH3. On the other hands, the 100 mg/L Pb(II) can be removed for 99% within an hours by WTS/nZVI composite 1:1 which was the fastest performance. In case of LHHW kinetics, k_r was 0.51 mg/L-min and K_{ads} was 0.028 L/mg ($R^2 = 0.934$) for Cr(VI). Moreover, k_r was 21.46 mg/L-min and K_{ads} was 0.00057 L/mg ($R^2 = 0.999$) for Pb(II). The main Cr(VI) and Pb(II) mechanism was reduction by nZVI. WTS was a carrier, dispersant, and sediment ($Cr_xFe_{1-x}(OH)_3$) supporter. The results suited with Langmuir isotherm. The q_{max} value was 63.29 mg/g, K_L value was 0.952 L/mg, and R^2 value was 0.998. The results suited with and pseudo second-order model more than Pseudo first-order model. The R^2 values were more than 0.993. All the best conditions were adapted in chromium removal from electroplating wastewater. The WTS/nZVI composite 1:1 can remove total chromium from electroplating wastewater for 99% within 14 hours.

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Anakhaphon Phiansi
October 2014

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LIST OF ABBREVIATIONS

Cr(III) = Trivalent chromium
Cr(VI) = Hexavalent chromium
Fe(III) = Iron(III)
g = gram
g/g = gram per gram
g/mg-min = gram per milligram per minute
H^+ = Proton
kg = kilogram
L/g = Littre per gram
L/mg = Littre per milligram
LHHW = Langmuir-Hinshelwood-Hougen-Watson
m^2/g = square meter per gram
mg/g = milligram per gram
mg/L = milligram per littre
mg/L-min = milligram per littre per minute
min^{-1} = per minute
mL/g = milliliter per gram
mV = millivolt
nm = nanometer
nZVI = Nano zero valent Iron
Pb(II) = Lead(II)
WTS = Water treatment sludge
WTS/nZVI = Water treatment sludge/nano zero valent iron

OPTIMAL CONDITION FOR HEAVY METALS REMOVAL FROM WASTEWATER USING WATER TREATMENT SLUDGE/NANO ZERO VALENT IRON COMPOSITE

INTRODUCTION

Heavy metals have been used as a significant substance for industrial manufacturing. There are lot of heavy metal release to an environment and continuously accumulate. Heavy metal toxicity harms organism. Chromium and lead are the main heavy metals mostly contaminated in water resource and have harmful effects to human. They are widely used in several industries especially in electroplating industry and alloy industry. (Swany *et al.*, 2002; Lv *et al.*, 2012; Jordan, 2010). The oxidation states of chromium which are almost use in the industry and can find in environment are chromium trivalent (Cr(III)) and chromium hexavalent (Cr(VI)). Cr(VI) can mobile and solute in aqueous solution easier than Cr(III), so this is a cause of carcinogenicity and toxicity occurring in the biosphere (Lv *et al.*, 2012). In Thailand, Department of Industrial Works decides the wastewater effluent standard from industries for Cr(VI) not more than 0.25 milligram per liter and Cr(III) not more than 0.75 milligram per liters. In addition, Lead in the environment has 2 types which are organic and inorganic lead. The acute toxicity of lead causes dysfunction in the kidneys, reproductive system, liver, and the brain and central nervous system and results in sickness or death. The amount of lead in the human body can be checked in urine and blood. There is a limit not over than 0.00001 grams per 10 deciliter blood.

There are several methods to remove chromium and lead out from the environment. The popular method is adsorption method because it is focus on cost effective reason. Thus, the plentiful waste materials from industrial estate and agricultural part are used to be an adsorbent. Water treatment sludge (WTS) which is a waste from the tab water production becomes the new choice because of its large amount production per year. WTS has a lot of surface area. There is the use of WTS for heavy metals removal. Moreover, WTS can be regenerated after adsorption process by EDTA, the chelating agent (Chiang *et al.* 2012). Other material which is used as an adsorbent because of its effectiveness is nanoscale zero valent iron (nZVI). nZVI is a substance used for contaminant elimination such as chlorine organic substance (Lien and Zhang, 1999) and heavy metals (Kanel *et al.*, 2006 and Kanel *et al.*, 2005). The two main mechanisms of nZVI to eliminate pollution substance are physicochemical adsorption and oxidation and reduction reaction. Moreover, there is the use of nZVI for the porous media modification. nZVI increased the pollution remediation effectiveness. On the other hands, there are some disadvantages of nZVI which are the stability of substance and its keeping process.

Therefore, this research studies about water treatment sludge (WTS) and nano zero valent iron (nZVI) composite developing in order to improve the effectiveness. Furthermore, this research studies about optimal condition to eliminate heavy metal such as chromium and lead by batch experiment, adsorption isotherm, and kinetics study.

OBJECTIVES

1. To study the optimal ratio of water treatment sludge/nano zero valent iron composite for hexavalent chromium removal

2. To study the appropriate condition and kinetics of hexavalent chromium removal by water treatment sludge/nano zero valent iron composite comparing with bare water treatment sludge.

3. To apply water treatment sludge/nano zero valent iron composite to lead removal from synthetic wastewater and compare with chromium removal

4. To apply water treatment sludge/nano zero valent iron composite to chromium removal from authentic wastewater

Scopes of work

1. All of the studies in this research were experimented in lab scale and batch experiment.

2. Potassium dichromate ($K_2Cr_2O_7$) and lead (II) nitrate ($Pb(NO_3)_2$) solution were used in the experiment as synthetic wastewater.

3. Water treatment sludge was modified by nano zero valent iron composite. The modification processes followed nano zero valent iron synthesis method.

4. Hexavalent chromium and lead concentration were analyzed in synthetic wastewater.

5. The authentic wastewater was from electroplating wastewater.

LITERATURE REVIEW

Chromium

Chromium is a naturally occurring element in rocks, animals, plants, soil, and volcanic dust and gases. It is one of the most heavy metals discharge made from the steel and alloy, electroplating, leather tanning process, mining, manufacturing of dye, paint and paper, and photography industries (Albadarin *et al.*, 2012 and Malkoc *et al.*, 2006). There are 2 types of chromium which is almost found in the environment; chromium trivalent (Cr(III)), which occurs naturally and is an essential nutrient, and chromium hexavalent (Cr(VI)), which is commonly produced by industrial processes. Cr(III) and Cr(VI) are both used in the manufacture part. Chromium exposure occurs from both natural and industrial sources. Cr(VI) ions persist as greatly soluble and highly toxic chromate ions ($HCrO_4^-$ or $Cr_2O_7^{2-}$) which means can mobile easily in water resource (Lv *et al.*, 2012). Figure 1 shows Cr(VI) species in aqueous solution in each pH. In addition, there are air emissions of Cr(III) and in the form of small particles or aerosols.

The hexavalent chromium has more toxic than the trivalent chromium 500 times (Levankumar et al., 2009). Cr(III) is an essential element in humans. It is essential to normal glucose, protein, and fat metabolism and is thus an essential dietary element. Some amount of Cr (VI) can be detoxified to Cr(III) by the body in order to increase Cr(III) levels in the body. The major target organ for Cr(VI) toxicity is the respiratory tract, for acute and chronic inhalation exposures. A case of acute exposure to Cr(VI) caused shortness of breath, coughing, and wheezing, while chronic exposure causes perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, and other respiratory. Moreover, a reason of cancer in the respiratory tract and digestive system is from the chronic exposure of Cr(VI). There are the studies of Cr(VI) effect in human and have clearly proved that Cr(VI) is a human carcinogen, resulting in an increased risk of lung cancer. Cr(VI) causes lung tumors in animal studies. On the other hand, Cr(III) ions are more stable, have a lower solubility and mobility performance in soils and water, and are determined as one of less harmful pollutant (Albadarin et al., 2012).

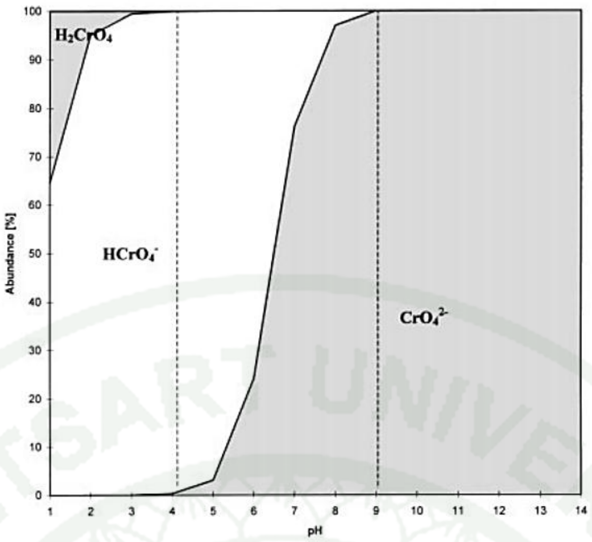

Figure 1 Cr(VI) species in aqueous solution at total Cr(VI) concentration 1×10^{-5} M and within pH 1±14

Source: Kotas and Stasicka (2000)

Thus, the amount of chromium in discharges must be decrease to an agreeable limit before releasing into the water resource in order to protect human health and the environment. Cr(VI) was categorized as a Group I human carcinogen by International Agency for Research on Cancer (IARC) and as a Group inhalation carcinogen by US Environmental Protection Agency (US EPA) (Levankumar *et al.*, 2009). The rate of releasing Cr(VI) must be lower than 0.05 mg/L in term of regulation (Albadarin *et al*., 2012) and 0.5 mg/L for Cr(III) (Levankumar *et al.*, 2009), but the rate of releasing total Cr (Cr(VI) and Cr(III)) must be lower than 2mg/L in term of regulation (Albadarin et al., 2012). In addition, there is the maximum contaminate level for chromium in drinking water established by the US EPA which is at 0.1 mg/L whereas these standards mean to the total concentration of the trivalent and hexavalent forms of dissolved chromium (Malkoc *et al*., 2006).

Lead

Lead is widely used in various industries such as electroplating, painting, batteries, appliances, etc. Lead severely affects human by touching, smelling, tasting, or using goods contaminated with lead. Thus, human obtains lead by direct and indirect ways. The toxic of lead is chronic, thus human do not act up suddenly. Lead particles in the environment can attach to dust and be carried long distances in the air. Lead containing dust can be removed from the air by rain and deposited on surface soil, where it may remain for many years. In addition, heavy rains may cause lead in surface soil to move into ground water and eventually into water systems (Mansoorian et al., 2014).

The toxic of lead causes abdominal pain, headache, anemia, irritability andin severe cases seizures, coma and death. The toxic of lead has two types; acute (intense exposure of short duration) and chronic (repeat low-level exposure over a extended period). The US Centers for Disease Control and Prevention and the World Health Organization annouce that a blood contains 10 μg/L or above lead is concerned. However, lead causes harmful health effects even at lower levels (Arshadi *et al.*, 2014).

Arshadi *et al.* (2014) used sineguelas waste supported by nano zero valent iron for removing lead (Pb(II)). Sineguelas was an effective carrier of nZVI. nZVI did not oxidized with air after 6 months. The mechanism of Pb(II) removal was Fe-Pb(II) redox reaction. Temperature affected the Pb(II) removal efficacy. The removal efficiency increased when the temperature increased.

Heavy metals removal

Table 1 Comparison of chemical process technologies for heavy metal ion removal

Process	Chemical/ Energy Input	Major Advantage	Major Disadvantage
Chemical precipitation	Precipitant/flocculant, acid, base, mixing, and fluid handling	Low metal concentration in the effluent are achieved	High chemical requirement, sludge disposal problem
Electrolytic recovery	Electrical energy	Lesser chemical consumption, recovery of pure metal is the added economic value	Energy intensive, high capital cost, reduced efficiency at dilute concentrations
Adsorption/ Ion exchange	Fluid handling unit/regenerating solution	Highly effective for removing metal ions to a very low concentration	Chemical regeneration requirement, fouling and corrosion of plant, disposal of exhausted adsorbent
Solvent extraction	Stripping solvent, make up extraction solvent	Selective heavy metal removal, continuous concentrated metal solution recovery	Capital costs, toxic solvent discharges
Menbrane	Extractant for liquid supported membrane	Selective heavy metal removal	Fouling and lesser durability of membranes

Source: Lewinsky (2007)

1. Chemical precipitation

Chemical precipitation is the most common technique for the removal of heavy metals from water and wastewaters. The most frequently used chemicals for precipitation of metals are lime caustic and sodium carbonates. The precipitation method has been used for the removal of iron, copper, zinc, tin, cadmium, and nickel from the effluents of metal finishing industries and for the removal of iron and aluminum in sewage water. Moreover, lime is used for the removal of lead and cadmium from water and wastewater. Moreover, there is the usage of sulfide to precipitate the heavy metals, but the disadvantage is that the sludge does not thicken well and sulfides are a potential odor and health hazard. Co-precipitation is another process where many metals are adsorbed on alum or iron flocs, but it has disadvantage of generating large quantities of sludge (Lewinsky, 2007).

Trivalent chromium (Cr(III)) can be removed by precipitation. Caustic soda or lime is used. Cr(III) is reduced in to chromium hydroxide form which is non-soluble. The appropriate pH is 8.5-9.5 as shown in figure 2 (Parson, 1965).

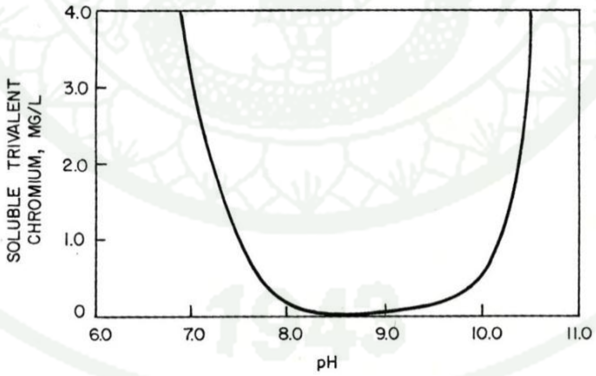

Figure 2 Soluble value of Chromium hydroxide

Source: Parsons (1965)

1.1 Sulfide precipitation

Most heavy metals form stable sulfides. Thus, sulfide precipitation is an outstanding method for the removal of metals. Sulfide precipitation gives lower residual metal concentrations than hydroxide precipitation. Further, metal sulfides usually settle faster and can be dewatered more readily than hydroxide sludge. Treatment with sulfide is most advantageous when used as a polishing step after conventional hydroxide precipitation or when the percentage of metal removals is very high (Lewinsky, 2007).

1.2 Carbonate precipitation

The carbonate precipitation method for the metals removal form wastewaters is very limited. There were the use of carbonate precipitation for cadmium(II) and lead(II) removal form electroplating effluents. At pH 7.5, the concentration of lead(II) and cadmium(II) were reduced to 0.60 and 0.25 mg/L, respectively (Lewinsky, 2007).

2. Evaporation

The evaporators are used chiefly to concentrate and recover valuable plating chemicals. Recovery is accomplished by boiling off sufficient water from the collected rinse stream to allow the concentrate to be returned to the plating bath. Both capital and operational costs for evaporative recovery systems are high. Chemical recovery and water reuse values must offset these costs for evaporative recovery to become economically possible. (Pinner, 1973).

3. Reverse osmosis

Reverse osmosis is the pressures driven membrane process by selective permeation of water through a semi permeable membrane. Reverse osmosis has wide spread popularity in the treatment of several diverse wastewaters. In plating chemical recovery applications, reverse osmosis units separate the valuable metal salts from rinse solutions. Reverse osmosis has also been successfully proved for the removal of Cr, Pb, Fe, Ni, Cu, and Zn (Sharma, 2014).

4. Electrodialysis

Electrodialysis is completed by placing cations and anion selective membranes alternatively across the path of an electric current. When the current is applied, the electrically attracted cations will pass through the cations exchanging membranes in one direction and the anions will pass through the anion exchanging membranes in the other direction. This technique would be as effective as reverse osmosis for the removal of these metal ions. The application of membrane process described is limited due to pretreatment requirements for the suspended solids removal. The methods are expensive require a higher level of technical expertise to operate (Lewinsky, 2007).

5. Ion exchange

. Ion exchangers are available selectively for certain metal ions. Resin is widely used as a media exchanger for ion exchange process The cation resins are mostly synthetic polymers containing an active ion group such as SO_3H. The natural materials such as zeolites are able to use as ion exchange media. The modified zeolites like zeocarb have greater affinity for metals like nickel and lead (Arshadi *et al*., 2014). The limitations on use of ion exchange for inorganic effluent treatment are the high cost of resins and the requirements for appropriate pretreatment systems and the sensitivity to pH of the wastewater. (Sharma, 2014).

Table 2 Selective removal of heavy metal ions by ion exchange

Metal ion	Ion Exchangers	Composition and functional groups
Pb(II)	Ethanotricarboxylate, 1,1-ddicarboxylate-2-etanophosphonate	Gel type copolymer of vinyl benzene chloeide, styrene, and divinyl benzene
	Polyacrylamidoglycol resin	Amide, OH, and carboxylic groups
	Clinoptilolite	Aluminosilicate structure
Cr(III,VI)	Amberlite IR-120	Polystyrenesulphone cation exchanger

Source: Lewinsky (2007)

6. Adsorption

Adsorption involves the accumulation (or depletion) of solute molecules at an interface. Adsorbent surfaces are often physically and/or chemically heterogenous and bonding energies may widely from one site to another. Adsorption involves accumulation of substance at an interface, which can either be liquid-liquid, gas-liquid, gas-solid, or liquid-solid as shown in figure 3. The material being adsorbed is termed the adsorbate and the adsorbing phase, the adsorbent. Chemical adsorption results in the formation of a monomolecular layer of the adsorbate on the surface through forces of residual valence of the surface molecules. Physical adsorption results from molecular condensation in the capillaries of the solid. In discussing the fundamentals of adsorption, it is useful to distinguish between physical adsorption, involving only relatively weak intermolecular forces. (Worch, 2012)..

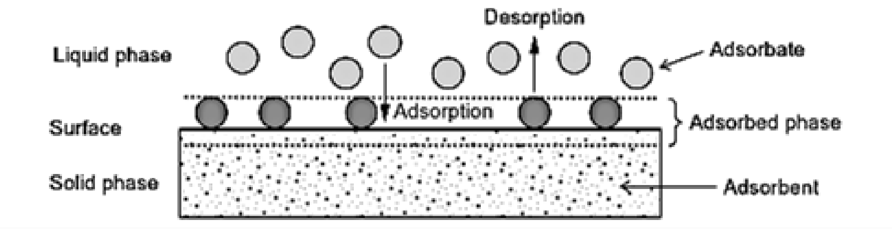

Figure 3 Basic terms of adsorption

Source: Worch (2012)

Table 3 Adsorption processes in water treatment process

Application Field	Objective	Adsorbent
Drinking water treatment	Removal of dissolved organic matter	Activated carbon
	Removal of organic micropollutants	Activated carbon
	Removal of arsenic	Aluminum oxide, iron hydroxide
Urban wastewater treatment	Removal of phosphate	Aluminum oxide, iron hydroxide
	Removal of micropollutants	Activated carbon
Industrial wastewater treatment	Removal or recycling of specific chemicals	Activated carbon, polymeric adsorbents
Swimming-pool water treatment	Removal of organic substances	Activated carbon
Groundwater remediation	Removal of organic substances	Activated carbon
Treatment of landfill leachate	Removal of organic substances	Activated carbon
Aquarium water treatment	Removal of organic substances	Activated carbon

Source: Worch (2012)

Adsorption is the potential way to decontaminate wastewater (Rafatullah *et al.*, 2010) because its design is simple, the operation is easy, and the system can be enlarged generally. Adsorption method has a high capacity to attach toxic substances with that can make pollutant decreases and the concentration of contaminant is decrease also (Albadarin *et al.*, 2012). Moreover, this method is uncomplicated to regenerate. It costs in low rate in every process. Most of all, it abstains from using harmful solvents (Worch, 2012; Rafatullah *et al*.; 2010; Albadarin *et al*., 2012).

The chemical adsorption and other heavy metals removal method such as precipitation method, lime coagulation, ion exchange, reverse osmosis and solvent extraction has many disadvantages like incomplete metal removal, high reagents and energy necessity, and occurring of toxic sludge which must be disposed in secure landfill. On the other hands, microbial reduction of Cr(VI) to Cr(III) is also possible. There is the using of biopolymers such as the microbial exopolysaccharides (Levankumar *et al.*, 2009).

Natural materials utilization is well known for the treatment of heavy metal waste as an alternative technology because of their interesting condition such as their high adjustability, metal selectivity and high uptake. There is using available biomaterials such as, Bengal gram husk, eucalyptus bark, saw dust, sugarcane bagasse, sugar beet pulp, coconut husk fibers, palm pressed fibers, waste tea, and Ocimum basilicum seeds (Levankumar *et al.*, 2009).

The activated carbon is used to be an adsorbent for chromium adsorption from wastewater. According to the study about chromium removal from municipal wastewater by using activated carbon, chromium removal efficiency is 55.55%-78.94% at low chromium concentration (0.09-0.19 mg/L). Moreover, chromium removal efficiency is 50.00%-99.00% at high chromium concentration (100-820 mg/L). Hence, the activated carbon is appropriate for high concentration chromium removal (Argo and Culp, 1972).

Chromium and lead precipitation by hydroxide

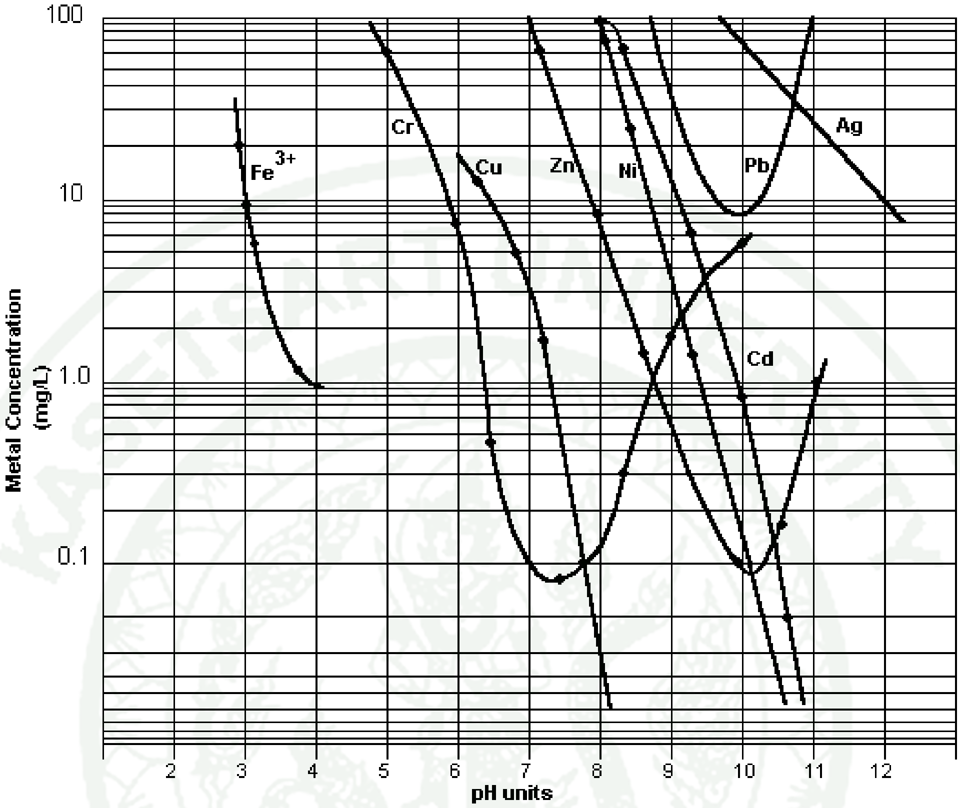

Figure 4 Heavy metals precipitation by hydroxide in each pH

Source: Hoffland Environmental Incorporation (2012)

Heavy metals are able to precipitate by hydroxide. Hence, pH value of the solution influences the existence of the dissolved heavy metals in the solution. The precipitation commonly follows the reaction below (equation 1). Heavy metals ion (M^{+n}) reacts with hydroxide ion (nOH^-). The heavy metals hydroxide occurs.

$$M^{+n} + nOH^- \leftrightarrow M(OH)_n \qquad (1)$$

Figure 4 shows the heavy metals precipitation by hydroxide in each pH. Many heavy metals such as chromium and zinc are amphoteric. They are able to be soluble (have a high concentration of dissolved heavy metals) at both alkaline and acid condition. According to the chromium and lead graph, the lowest concentration of dissolved chromium and lead are 0.07 and 8 mg/L at pH 7.5 and 10, respectively. It implies that chromium and lead inclines to precipitate at pH 7.5 and 10, respectively. (Armenente, 1997)

Water treatment sludge

Water treatment sludge (WTS) are primarily sediment (including silica), aluminum, iron, or calcium oxide/hydroxides, activated carbon, and lime removed from raw water during the water purification process (Agyin-Birikorang *et al.*, 2007). Water treatment sludge may also carry pathogens, organohalogen contaminants (Sotero-Santos *et al.*, 2005). The Scanning Electron Microscope (SEM) images of water treatment sludge are shown as Figure 5.

Coagulation, flocculation, sedimentation, and filtration are the processes used in water treatment to remove turbidity, color, taste, and odor from raw water. The small particles were combined and formed the larger aggregates by coagulation and flocculation. Generally, ferric chloride ($FeCl_3$) or alum ($Al_2(SO_4)_3{\cdot}14H_2O$) are used as a chemical coagulant. The residuals resulting from the use of the coagulants are referred to as aluminum-based WTS (Al-WTS) and iron-based WTS (Fe-WTS) (Irawan *et al.*, 2011). In addition, there are calcium-based WTS (Ca-WTS) which is produced in water-softening facilities where lime is used to decrease hardness.

There is the increase of water treatment facilities because of a consequence of the population expansion. Thus, the generation of WTS is increased and that requires appropriate methods of disposal. The WTS can be disposed in 4 ways;

1) directly to a receiving stream

2) to sanitary sewers

3) to a landfill, assuming that the WTS contains no free-draining water and does not have toxic characteristics as defined by the toxicity characteristic leaching procedure (TCLP) test

4) by land application such as phosphorus immobilization in soils

There is the use of WTS in order to reduce pollutants. It depends on several factors, including source water characteristics, water treatment methods, and WTS storage time prior. Each water treatment facility uses unique source water and different treatment chemicals and processes, producing WTS with different physical and chemical compositions and sorption capability. Irawan *et al.* (2011) studied about boron removal using aluminum based water treatment residuals (Al-WTS). Al-WTS composed of Al_2O_3, Fe_2O_3 and SiO_2. An amount of alumina affected boron adsorption. The optimal pH was 8.2-8.5. The adsorption mechanism was a monolayer adsorption which was a combination of electrostatic interactions and van der Waals interaction.

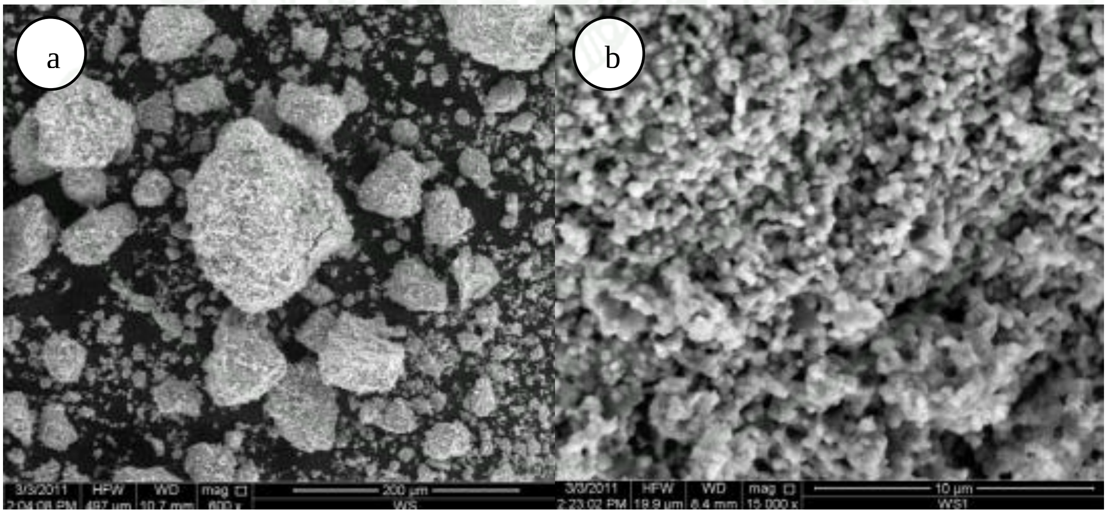

Figure 5 Water treatment sludge by SEM (a) Water treatment sludge particle (600x) and (b) Water treatment sludge particle (15,000x) taken by SEM, respectively

Source: Kizinievič *et al.* (2013)

Nano zero valent iron (nZVI)

nZVI can be used for environmental remediation of contaminants in soils, sediments, and groundwater. nZVI particles are an electron donor for inorganics reduction. Moreover, nZVI particles are able to make surface transmitted complexes, which can immobilize the inorganic contaminants. nZVI can be simply used for remediation of trace metals and metalloid contaminants in groundwater because of its small size (Huang *et al.*, 2013).

nZVI is used to be a material for site remediation such as chlorinated compound (Li *et al.*, 2011), 2,4-DPC (Wang *et al.*, 2011). Actually we can find the form of Fe in Fe(II) and Fe(III) which is stable in environment condition. In case of nZVI, it is in unstable form which can easily react with oxygen. Hence, it has a high ability in toxic transformation from toxicity to less toxicity. There are 3 way possible to remove the pollutant by nZVI.

1. Ion reduction at the surface of nZVI

2. Catalytic reduction

3. Adsorption on corrosion product

The substance like nZVI is a reducing reagent which can react with dissolved oxygen (DO). As the equations below, nZVI oxidize to ferrous iron (Fe(II)) ions and the electrons that are released are available to reduce other compounds. This process can be accelerated by changing the solution and/or materials component inhibition by coating or adding catalyst (Keane, 2009). Equation 2 shows the reaction between Fe_0 and O.

$$2Fe_0(s) + 4H^+(aq) + O_2(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O\ (l) \qquad (2)$$

The order of the best adsorption of nZVI with heavy metals, respectively are As>Cr>Cu>Hg>Pb>Zn>Cd>Ni and especially Cr(VI) can react with nZVI more than one mechanism such as ion reduction, adsorption, and co-precipitation. In consideration of organic compound, nZVI has the qualification in dissolved metal toxification reduction which these metals is reduced the oxidation state and co-precipitated with ferric oxyhydroxide on nZVI surface (Wang *et al.*, 2011).

Table 4 General environmental contaminants transformed by nanoscale iron particles

Chlorinated methanes	**Heavy metal ions**	**Other polychlorinated hydrocarbons**
Carbon tetrachloride	Mercury	PCBs
Chloroform	Nickel	Dioxins
Dichloromethane	Silver	Pentachlorophenol
Chloromethane	Cadmium	
Chlorinated benzenes	**Organic dyes**	**Other organic contaminants**
Hexachlorobenzene	Orange II	N-nitrosodimethylamine
Pentachlorobenzene	Chrysoidine	TNT
Tetrachlorobenzenes	Tropaeolin O	
Trichlorobenzenes	Acid Orange	
Dichlorobenzenes	Acid Red	
Chlorobenzene		

Source: Keane (2009)

About using iron particle for chromium removal, there was the using of thin iron wire for chromium removal. It was found that wastewater contained 14 mg/L chromium can be reduce 50% in 4 hours. The reduction speed increased at low pH condition. In addition, there was the using of casting iron in high concentration chromium wastewater treatment at 534 mg/L by plug flow reactor. The result indicated that chromium reduction completed when the hydraulic retention time is 98 minutes. The reaction occurred efficiently at pH 2 (Chen *et al.*, 2008). In addition, cadmium(II) was removed by nZVI (Borapai *et al.*, 2011). The adsorption mechanism was chemisorption at the surface.

Silica material improvement by nZVI

While nZVI particles reduced Cr(VI), the sediment of $Cr_xFe_{1-x}(OH)$ or $FeOH_2$ occurred and attached to the surface of nZVI. The active area of nZVI decreased and the Cr(VI) removal efficiency also decreased. Silica was an appropriated materials for sediment support because surface area of silica had silanol group which was a buffer and splitted itself to silicon monoxide and proton as shown in equation 3 (Kelsey and Seeds, 1972).

$$\equiv SiOH \leftrightarrow \equiv SiO^- + H^+ \tag{3}$$

Silano group binded with $Fe(OH)_2$ sediment and occurred as silicon monoxide. Silicon monoxide on the silica suface can attach $Fe(OH)_2$ and $Cr_xFe_{1-x}(OH)$ sediment as shown in Figure 6.

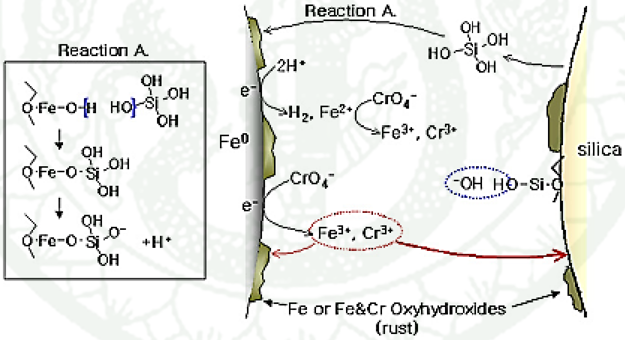

Figure 6 Cr(VI) reduction process by nZVI-silica composite

Source: Kelsey and Seeds (1972)

Sun *et al.* (2014) studied about two solvents reduction technique which was used to remove Cr(VI) from groundwater using nZVIs incorporated inside the channels of SBA-15 (mesoporius silica) rods. The mechanism of Cr(VI) removal by nZVIs/SBA-15 was absorption and reduction. Cr(VI) were first absorbed by the composites, saturated into the silica pores. Then Cr(VI) were reduced to Cr(III) by the nZVI. Cr(VI) can removed propeciously by NZVIs/SBA-15 in low pH value. Humic acid in groundwater affected the removal efficiency of Cr(VI). Figure 7 shows the mechanism of nZVI/SBA-15 in order to remove Cr(VI).

Oh *et al.* (2007) found that the mixing of non-binding silica and nZVI made the Cr(III) reacted with nZVI directly. Then the surface area of nZVI and its efficiency decrease. To prevent, the obstacles of Cr(VI) removal, nZVI binded with silica was the best way in order to be the reducing agent, the sediment producer, and the sediment supporter. All forms of chromium, which were Cr(VI), Cr(III), and Cr(III) sediment, were eliminated.

Moreover, the surface of nZVI is improved by dissolving the ferric chloride in ethanol. It informed the increase of surface area of nZVI (Wang et al., 2009)

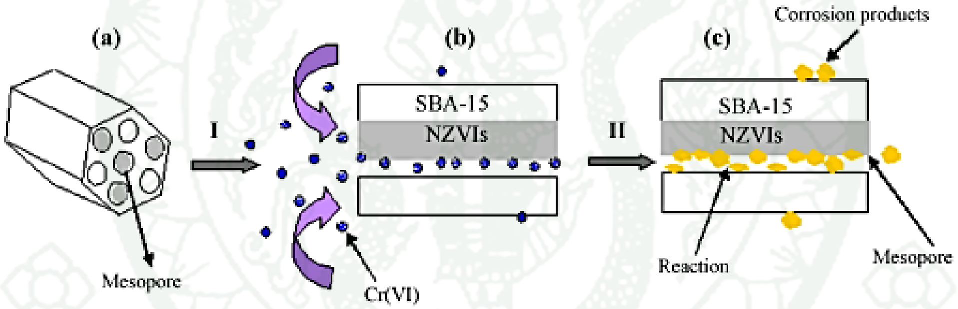

Figure 7 The Cr(VI) removal mechanism by nZVI/SBA-15. (a) nZVIs/SBA-15, (b) chromate was saturated into the mesopore, and (c) reduction reaction between the nZVI and Cr(VI) in the mesopore.

Source: Sun *et al.* (2014)

Pseudo first-order and pseudo second-order kinetics

Lagergren’s first-order rate equation described the adsorption rate on the base of the adsorption capacity (equation 4).

$$\frac{dq}{dt} = k_1 (q_e - q) \tag{4}$$

Where q is the metal concentration in solid phase at time t, and q_e is the equilibrium metal concentration in solid phase.

In order to distinguish kinetic equations based on concentrations in solution from kinetics equations based on adsorption capacities of solids, Lagergren's first-order rate equation has been called pseudo first-order

Integration of equation (boundary condition; t = 0, q = 0 and t = t, q = q) gives as equation 5.

$$q = q_e (1-\exp(-k_1 t)) \tag{5}$$

which can be expressed in linear form as equation 6.

$$\ln(q_e-q) = \ln q_e - k_1 t \tag{6}$$

q_e and k_1 parameters can be determined by non linear procedure fitting or by linear regression using plots $\ln(q_e - q)$ versus t obtained for different initial metal concentrations. The q_e values then contrasted with experimental values and if large difference exist, the reaction cannot be classified as pseudo first-order although high regression coefficients were obtained for the linear plots (Kotrba *et al.*, 2011).

Pseudo second-order model is derived assuming a second order dependence of the sorption rate on available sites as equation 7.

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{7}$$

Integration of equation (boundary conditions; t = 0, q= 0 and t = t, q = q) gives as equation 8.

$$q = q_e \left(1 - \frac{1}{1+q_e k_t t}\right) \tag{8}$$

which can be stated in the linear form as equation 9.

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (9)$$

Pseudo second-order parameters (q_e and k_2) were determined by plotting t/q against t (Albadarin *et al.*, 2012; Ahmad *et al.*, 2011).

Adsorption Isotherm

The Langmuir and Freundlich model isotherms were used for discovering the equilibrium data of adsorption in order to find out the correlation between solid phase and aqueous concentrations at equilibrium.

1. Langmuir isotherm

The Langmuir isotherm is based on 4 hypotheses which are (Worch, 2012)

1.1 All the surface of adsorbent is the same condition and the entire adsorption site are equal in amount.

1.2 Adsorbed molecules can’t interact anymore.

1.3 All adsorption happen at all same condition

1.4 At the maximum adsorption, only one layer has formed.

The Langmuir adsorption isotherm is shown in equation 10.

$$q = \frac{q_{max} b c_e}{1+bc_e} \qquad ...(10)$$

Where q_{max} (mg/g) and b (L/mg) are Langmuir constants connected to the capacity and energy of adsorption.

The basic attribute of the Langmuir isotherm can be predicted the affinity between sorbate and sorbent by dimensionless separation factor (R_L) (Albadarin *et al.*, 2012 and Malkoc *et al.*, 2006).

$$R_L = \frac{1}{1+(q_{max} \times b)c_0} \tag{11}$$

In equation 8, the R_L parameter shows the shape of the isotherm as follows: RL >1 means unfavorable; RL = 1 means linear; 0<RL<1 means favoralble; RL = 0 means irreversible.

2. Freundlich isotherm

The Freundlich equation is shown as equation 12

$$q_e = k_f c_e^{1/n} \tag{12}$$

Where K_F and1/n are the Freundlich model constants associated to the capacity and intensity of the adsorption respectively. A favorable adsorption almost has Freundlich constant n between 1 and 10. A higher value of n (smaller value of 1/n) indicates stronger interaction between the absorbent and adsorbate (Malkoc *et al.*, 2006).

Langmuir-Hinshelwood-Hougen-Watson Kinetics

The Langmuir-Hinselwood-Hougen-Watson (LHHW) method of generating rate models based on Langmuir adsorption was systematically developed by Hougen and Watson. It has had some success in the transient case but it works best at steady state. The LHHW methodology can be summarized in the following steps (Hayes and Kolaczkowski, 1998).

Step 1: Propose a mechanism base on; (a) Langmuir adsorption, (b) surface reaction between adsorbed intermediates, and (c) desorption. Proposing a mechanism for the reaction can be difficult and is often based on assumption and experimental data. Any information which is available about the nature of the surface intermediates should be used at this stage.

Step 2: Assume that one of the steps in the mechanism is intrinsically slow. This step is said to be the rate determining step (RDS). It must be emphasized that at steady state, the actual rate at which each step in the mechanism proceeds is the same. Intrinsically slow implies that the values of the appropriate rate constants for this step are small. The other steps are assumed to be in equilibrium. This is not a true equilibrium because actually all steps have the same finite rate. However, if the equilibrium steps are intrinsically very fast, they will not be far from equilibrium and the assumption of a single rate determining step will be valid.

Step 3: Write the overall rate of reaction in terms of the rate determining step. This rate expression will contain surface concentration terms of adsorbed intermediates.

Step 4: Eliminate the surface (adsorbed) concentration terms from the expression using the steps in the mechanism which are assumed to be in equilibrium. The final rate expression is expressed in terms of gas phase concentrations.

However, the Hougen-Watson concept was very successfully applied since a large variety of catalytic reactions could be described under the steady state conditions. Usually, different rate equations of the Langmuir-Hinshelwood type are able to describe the experimental data with similar quality, which results from the large number of kinetic parameters making the mathematical expressions very flexible. This implies that a fit of experimental data by these rate expressions does not give any final evidence for a certain reaction mechanism. If more detailed information on the reaction mechanism is desired for the purpose of interpreting the behavior of catalysts, the steady state experiments to which the Langmuir-Hinshelwood equations exclusively can be applied must be supplemented by non-steady state experiments. (Baerns, 2004).

The Hougen-Watson formula is widely used, but has its limitations (Helfferich, 2004). Specifically, it assumes that,

1. All catalytic sites are alike

2. Each adsorbed molecule occupies one site.

3. The surface reaction occurs in, or can be reduced to, a single step.

4. Adsorption kinetics and equilibrium obey Langmuir equations.

5. A single adsorption, desorption, or reaction step controls the rate.

6. Tubulations cover only reactions with some simple stoichiometries.

The initial degradation rates (r_0) were used in the linear LHHW model plots of the inverse initial degradation rates ($1/r_0$) versus the inverse initial equilibrium atrazine concentrations ($1/C_0$) (Naimi-Joubani *et al.*, 2014). Equation 13 shows the linear equation of LHHW kinetics.

$$\frac{-1}{r_0} = \frac{1}{K_{ads}C_0} - \frac{1}{k_r} \tag{13}$$

where k_r = reaction rate constant (mg/L-min)
K_{ads} = adsorption equilibrium constant (L/mg)
C_0 = initial equilibrium concentration of pollution (mg/L)

The four-point differentiation formula was applied to estimate the initial degradation rate (r_0) for each initial concentration of the pollutant. The r_0 calculation concerns only the experimental data obtained during the first minutes of reaction time in order to minimize variation as a result of competitive effect of intermediates, pH changes, etc. (Li *et al.*, 2011). Equation 14 shows r_0 calculation.

$$r_0 = \frac{(-3C_0 + 4C_1 - C_2)}{2\Delta t} \tag{14}$$

where r_0 = initial photocatalytic degradation rate (mg/L-min)

C = concentration of atrazine at reaction time t (mg/L)

$\Delta t = t_2 - t_1$ (min)

MATERIALS AND METHODS

Materials

1. Sodium borohydride ($NaBH_4$) (AR grade)
2. Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) (AR grade)
3. Potassium dichromate ($K_2Cr_2O_7$) (AR grade)
4. Lead (II) nitrate ($Pb(NO_3)_2$) (AR grade)
5. Ethyl alcohol (AR grade)
6. Acetone (AR grade)
7. Diphenyl carbazide (AR grade)
8. DI water
9. Water treatment sludge (WTS) from Bangkhen water treatment plant
10. Shaking incubator
11. Nylon filter 0.45 µm
12. Syringe 10 mL
13. Micropipette
14. pH meter (Mettler Toledo, DG 115-SC)
15. UV-VIS spectrophotometer (PerkinElmer, Lambda 650)
16. Flame Atomic Absorption Spectrometer (FAAS) (Perkin Elmer, Pinaacle 900F)
17. Scanning Electron Microscope (SEM) (Quanta 450 FEI)
18. Surface Area and Porosity Analyzer (BET) (BEL Japan, BELSORP)
19. Mechanical stirrer (IKA, RW 20 digital)
20. Zetasizer (Malvern, Nano ZSP)
21. Hot plate stirrer
22. Vaccum pump (Vaccumbrand, CVC 2)
23. Desiccator
24. Sieve mesh 500 µm
25. Hot Oven (Memmert, UNE 200)
26. Analytical balance 4 digits (Mettler Toledo, XS 204)
27. Scientific glassware

Methods

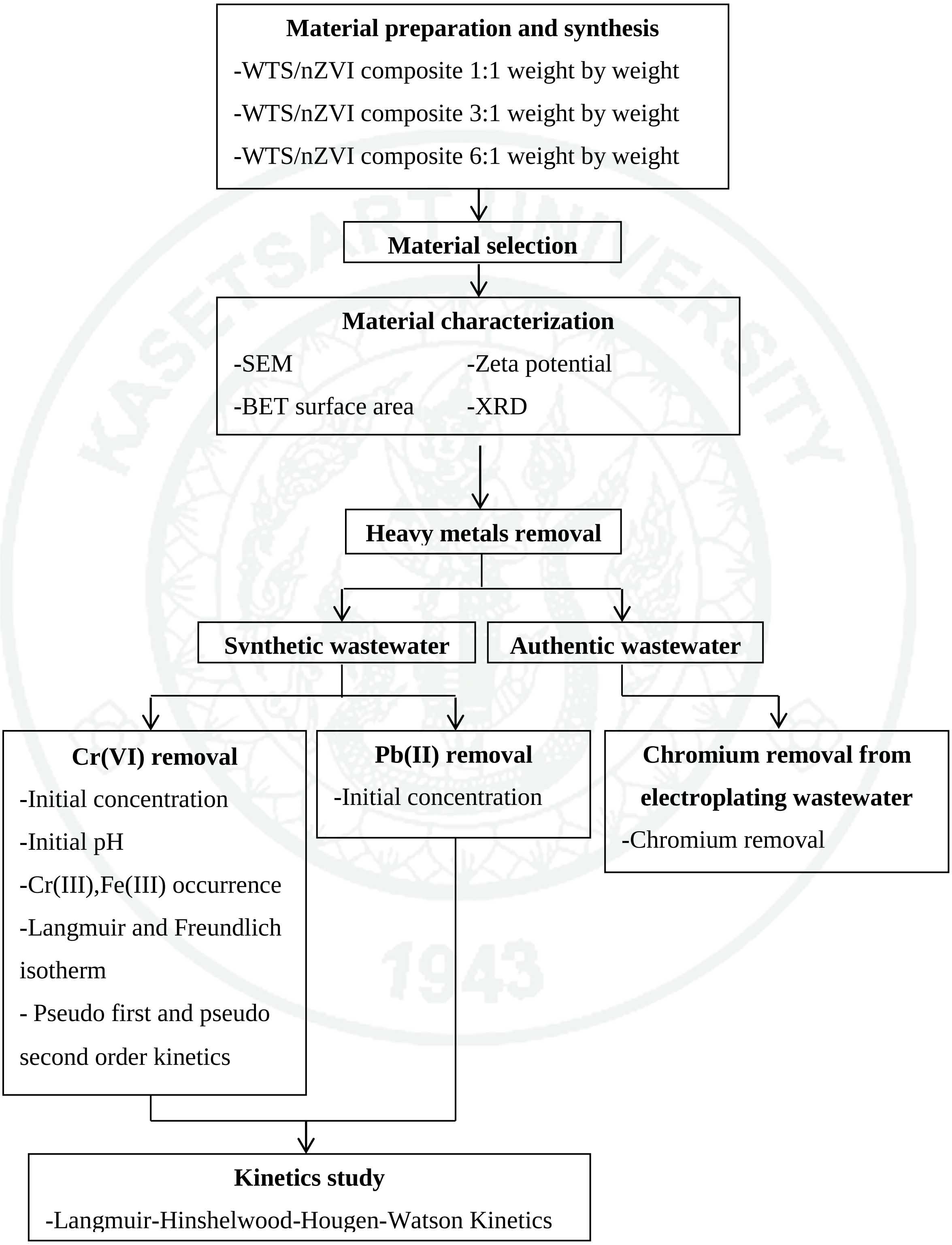

Figure 8 Schematic diagram of the experiment

1. Materials Preparation and characterization

1.1 Water treatment sludge (WTS) collection and preparation

The WTS was collected from Metropolitan Waterworks Authority, Thailand. The water treatment sludge was a sludge from water treatment process which was gone through the filter press; the dewatering machine (Figure 9a). The water treatment sludge had brown-grey color, was unshaped, and the size was about 0.2×0.4 square meters. Then the water treatment sludge was crushed (Figure 9b) and dried at 105°C in the oven (Irawan *et al.*, 2011). Then it was sieved by 500 µm sieve mesh.

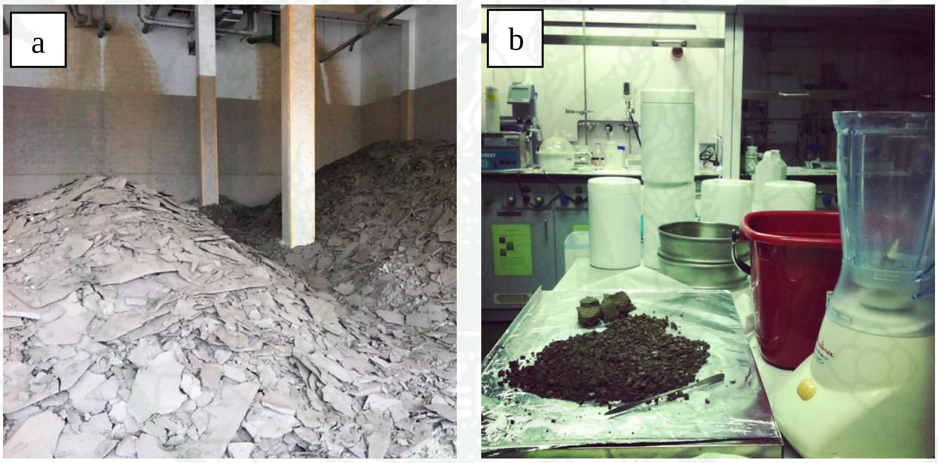

Figure 9 WTS collection a) WTS at filter press site, b)WTS crushing

1.2 Water Treatment Sludge (WTS)/Nano Zero Valent Iron (nZVI) composite synthesis

WTS/nZVI particles were synthesized by following the method of Shu *et al.*, 2007. 0.6 M iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) was prepared (Figure 11a). Then WTS (Figure 12a) was added into $FeCl_3$ solution and sonicated for 30 minnutes. After that, it was gradually dropped into an excessive 0.8 M sodium borohydride ($NaBH_4$) solution in three necks double jacketed flat bottom flask at 15°C, under nitrogen atmosphere. The solution was stirred by the mechanical stirrer at

400 rpm (Jiemvarangkul *et al.*, 2011) (Figure 11b). The reaction of $FeCl_3{\cdot}6H_2O$ and $NaBH_4$ is showed as a chemical equation 15 and in figure 10.

$$Fe(H_2O)_6^{3+} + 3BH_4^{-} + 3H_2O \rightarrow Fe_0{\downarrow} + 3B(OH)_3 + 10.5H_2 \qquad (15)$$

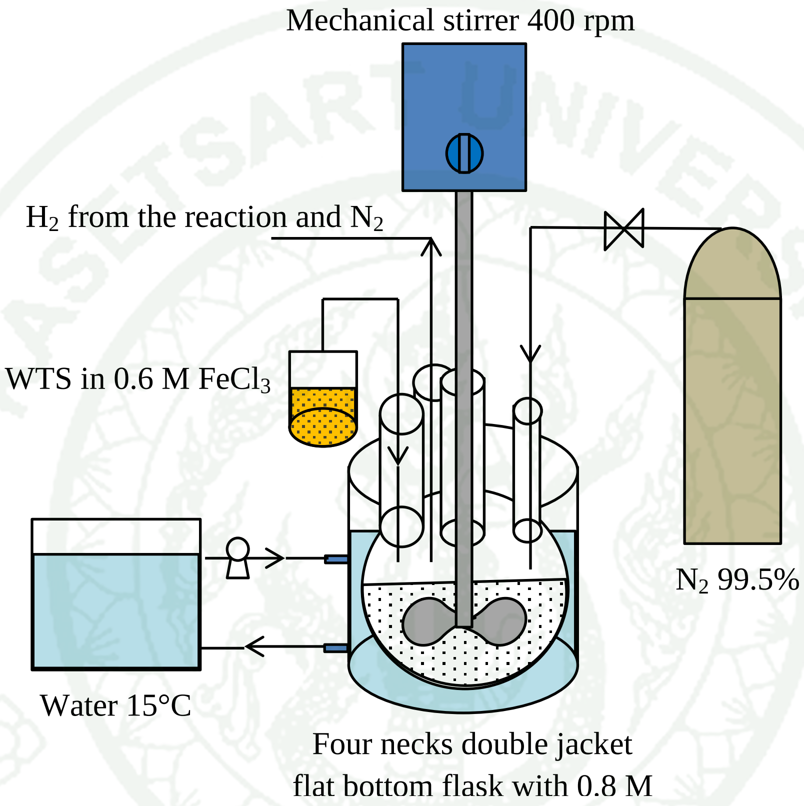

Figure 10 A diagram of WTS/nZVI synthesis

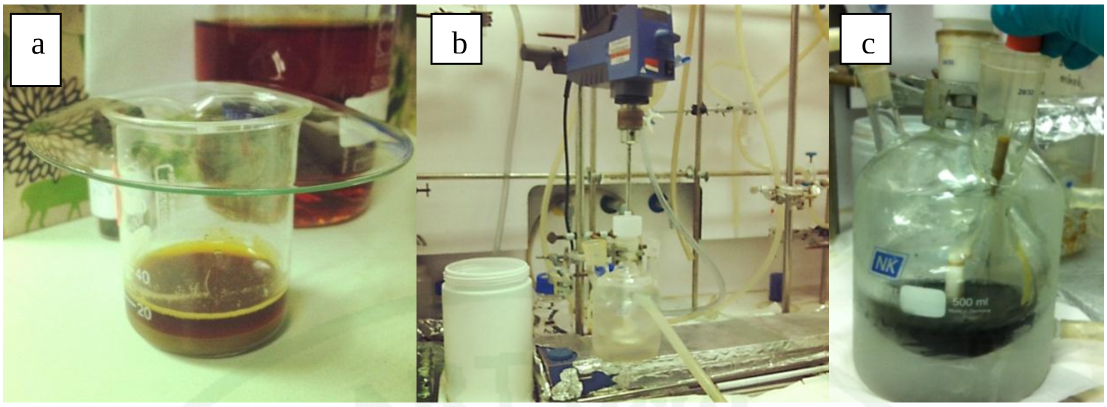

Figure 11 WTS/nZVI synthesis a) WTS in $FeCl_3$, b) WTS/nZVI composite symthesis in the three necks double jacketed flat bottom flask, c) WTS/nZVI composite got from synthesis process

After that, black particles were occurred (Figure 11c) and washed by deionized water until borohydride ions were all washed out. The magnet was used to separate nZVI particle from the solution. The ethanol solution was used to be the last wash. These all process did under the nitrogen atmosphere in order to prevent the oxidation of nZVI. Finally, the ethanol is evaporated by heat at 80°C. The dry nZVI particles are crushed and collected into the bottle with purged nitrogen gas and keep in the Desiccator. The finished WTS/nZVI composite was shown in figure 12b.

An amount of $FeCl_3 \cdot 6H_2O$ and $NaBH_4$ for nZVI synthesis were calculated. An amount of nZVI was fix at 1.5 g for every ratio of WTS/nZVI composite. The ratio of an amount of $Fe(H_2O)_6^{3+}$: BH_4^- : Fe_0 was equal to 1:3:1.

In conclusion, 1.5g of nZVI was prepared by 0.6 M $FeCl_3 \cdot 6H_2O$ solution 44.76 mL and 0.8 M $NaBH_4$ solution 150 mL (excess). The water treatment sludge added is in a different WTS/nZVI ratio; 1:1, 3:1, 6:1, respectively. The amount of nZVI/sludge is in the table 5 below

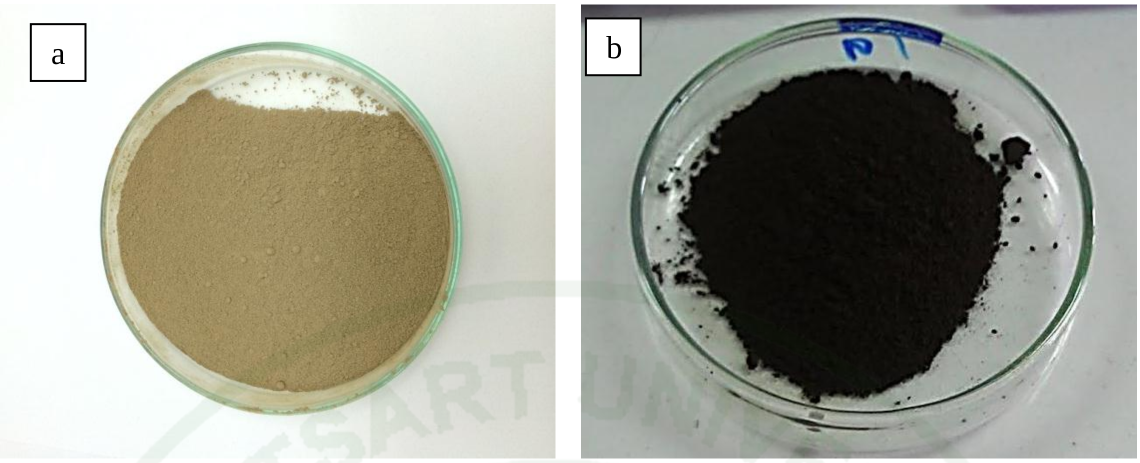

Figure 12 The materials a) bare WTS, b) WTS/nZVI composite 1:1 weight by weight

Table 5 The amount of nZVI and sludge in each WTS/nZVI composite ratio

WTS/nZVI composite ratio	**An amount of sludge (g)**	**An amount of nZVI (from calculation) (g)**
1:1	1.5	1.5
3:1	4.5	1.5
6:1	9.0	1.5

All ratio composite are test the adsorption with Cr(VI) 10 mg/L and were chose the one which had the best performance.

1.3 Water Treatment Sludge (WTS)/Nano Zero Valent Iron (nZVI) composite analysis

1.3.1 Scanning electronic microscope (SEM)

Surface morphology and the particle dispersion of the materials were seen by scanning electron microscope with energy dispersive x-ray (SEM-EDX) (Quanta, 450 FEI). These samples were fixed at carbon tape to analyze (Lv *et al.*, 2012).

1.3.2 Zeta Potential

The pH of deionized water was adjusted to 2-12 by 0.5 M H_2SO_4 or 0.5 M NaOH. Then the materials were put in the solution and shaked for particle dispersion. Zeta potential value was analyzed by zetasizer.

1.3.3 Surface Area and Porosity Analyzer (BET)

The principle of Brunauer–Emmelt–Teller (BET) is to analyze an amount of nitrogen gas adsorbed on a surface of a material. Before analyzing, gases except nitrogen gas and have a boiling point more than nitrogen gas are eliminated by heating at 250°C for 2 hours by BEL Japan, BELSORP. Then the equipment proceeds according to the BET equation. The results are displayed by surface area value and porosity value (Phuengprasop *et al.*, 2011).

1.3.4 X-ray diffraction (XRD)

The technique of x-ray diffraction is used for studying on crystal structure of solid atom and components of the materials. The materials before and after reaction are deposited in the sample holder for XRD analysis. The analysis is executed with a CuKα radiation at a scanning rate of 8° min^{-1} in the 2θ range from 5°to 85°to ascertain the arrangement of these particles (Lv *et al.*, 2012).

2. Heavy metals removal experiment

2.1 Hexavalent chromium (Cr(VI)) removal study

In the case of hexavalent chromium (Cr(VI)), batch experiments were required varied in 4 parameters; the ratio of WTS/nZVI in the composite, the materials, the initial Cr(VI) concentration, and initial pH (Lv *et al.*, 2012). In addition, Pb(II) was experimented to compare the efficiency with Cr(VI) by varying the initial concentration and find its kinetics.

In the effect of the ratio of WTS/nZVI in the composite, there are 3 WTS/nZVI ratio concerned which were 1:1, 3:1, and 6:1 weight by weight WTS and nZVI, respectively. The WTS/nZVI composite was added 0.1 g in chromium solution 100 ml in Erlenmeyer flask. The flasks are shaked in the shaking incubator 100 rpm (Lv *et al.*, 2012). The samples were collected every 15 minutes in the first 2 hours and then every 30 minutes until the Cr(VI) concentration was in the equilibrium condition. Afterwards, all samples were filtrated with 0.45 µm filter membrane and were diluted in 50 ml volumetric flask (Figure 13a). The 2 ml diphenylcarbazide and H_2SO_4 was added to give purple color at the pH of 2±0.5 After 10 minutes, the solutions turned purple (Figure 13b) and then measure the absorbance with UV-VIS spectrophotometer at 540 nm. The calibration curve is used to interpret the concentration removed (US EPA, 1992). The experiment was done duplicated.

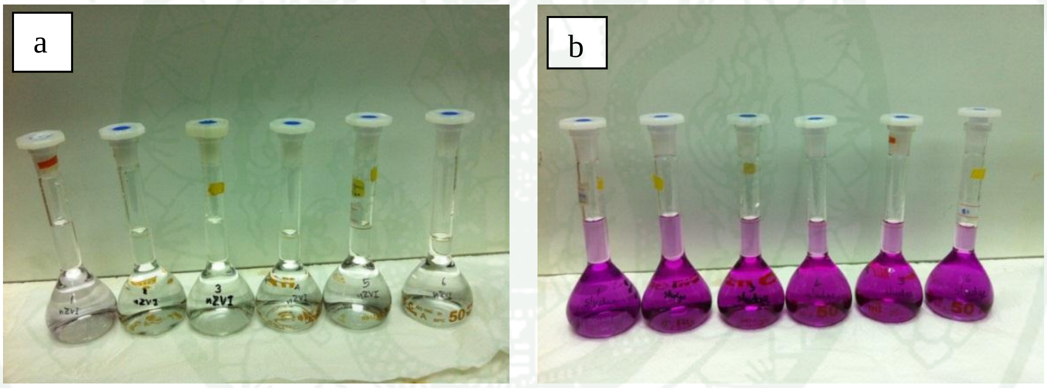

Figure 13 Cr(VI) solution a) Cr(VI) diluted solution at each time collected before adding diphenylcarbacide b) After adding diphenylcarbacide, color formation of Cr(VI) and diphenylcarbacide occurred

The WTS/nZVI ratio with the best performance was used to be a material in other experiment. The materials which were WTS, commercial nZVI, and WTS/nZVI composite 1:1 In the effect of the initial concentration, the concentration of Cr(VI) solution were varied into 10, 20, 40, 60, and 80 mg/L compared with bare WTS. In addition, in the effect of the initial pH, the pH of Cr(VI) solution are varied into 3 pH; 3, 5.8, and 11. The experiment was done duplicated.

2.2 Trivalent chromium (Cr(III)) study

Cr(III) concentration was calculated from the difference of total chromium concentration and Cr(VI) concentration. Total chromium concentration was analyzed by Flame Atomic Adsorption Spectrometer (FAAS) at wavelength 357.87 nm.

2.3 Residual iron study

Residual iron concentration was analyzed by Flame Atomic Adsorption Spectrometer (FAAS) at wavelength 248.33 nm.

2.4 Lead (Pb(II)) removal study

The concentration of Pb(II) solution were varied into 100, 500, 1000, 1500, and 2000 mg/L. The samples were collected every 15 minutes in the first 2 hours and then every 30 minutes until the Pb(II) concentration was in the equilibrium condition. Pb(II) concentration was analyzed by Flame Atomic Adsorption Spectrometer (FAAS) at wavelength 283.31 nm. The experiment was done duplicated.

The heavy metal removal capability of the WTS/nZVI composites was estimated at several parameters to stand for the real natural circumstance and the happened effects on adsorption. Equation 16 and 17 were calculated for finding the equilibrium adsorbed concentration (q_e) and the removal efficiency (ŋ), respectively (Lv *et al.*, 2012).

$$q_e = (C_0 - C_e) \times V/M \tag{16}$$

$$\eta = (C_0 - C_e)/C_e \times 100\% \tag{17}$$

Where; C_0 is the initial concentration of heavy metal solution, C_e is the equilibrium concentration of heavy metal solution, V is the solution’s total volume, and M is a mass of the adsorbent

3. Langmuir-Hinshelwood-Hougen and Watson kinetics study

The heterogeneous reaction kinetics had been validated with the Langmuir-Hinshelwood-Hougen and Watson (LHHW) model. This model covered the reaction occurring at the solid-liquid interface and the adsorption property of pollutant on the material surface (Idris *et al.*, 2011).

4. Adsorption Isotherm Study

The Langmuir model describes the reaction that adsorption happens on a monolayer where all adsorption sites are the same equivalent. The Lamgmuir model was shown in equation 10.

On the other hand, the Freundlich isotherm assumes the adsorption that occurs on a heterogeneous surface which is shown as equation 11.

5. Pseudo-first-order and Pseudo-second-order kinetic equation study

5.1 Pseudo-first-order kinetic equation

The pseudo first order rate equation can be indicated as equation 6 (chen *et al.*, 2013).

5.2 Pseudo-second-order equation

Adsorption kinetics is described by the pseudo-second-order model as equation 9.

6. Total chromium removal from Electroplating Wastewater

The wastewater was collected from Sum Hitechs Company co.ltd., Navanakorn Industrial Estate, Pathumthani, Thailand. 0.1 g WTS/nZVI composite was added into 100 ml wastewater. The samples was collected every 2 hours. The total chromium concentration was analyzed by Flame Atomic Adsorption Spectrometer (FAAS) at wavelength 357.87 nm.

RESULTS AND DISCUSSION

1. Material preparation and characterization

1.1 Scanning Electron Microscopes (SEM)

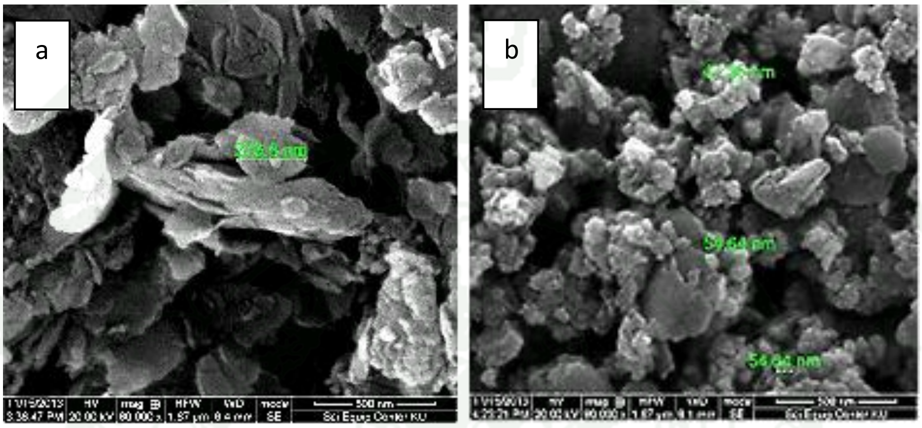

Figure 14 SEM images of a) water treatment sludge (WTS), b) water treatment sludge/nano zero valent iron (WTS/nZVI) composite 1:1 weight by weight at 80000× magnification.

The morphologies of WTS and WTS/nZVI composite 1:1 weight by weight were presented in Figure 14. The shape of the surface of WTS (Figure 14a) was like a flake, thus there was a lot of surface area appropriated to adsorb pollutants. After the synthesis process, the round shape particles of NZVI were dispersedly attached around the surface of WTS with the size ranging from 45 to 55 nm (Figure 14b).

1.2 Zeta Potential

Zeta potential values indicated the type of charges around the surface of the particle. Figure 15 and Table 6 displayed zeta potential values of WTS and WTS/nZVI composite 1:1 at pH2-12. The results indicated that zeta potential of WTS and WTS/nZVI 1:1 were all the negative charges at the surface of both materials in every pH value. The zeta potential values were until -14 to -18 mV for WTS/nZVI 1:1

and -6 to -24 for WTS. They were less than -20 mV for pH6 to pH12. This indicated that WTS had electrostatic repulsion of anion stronger than WTS/nZVI 1:1 under base condition. However, both materials were able to attach with cation pollutant.

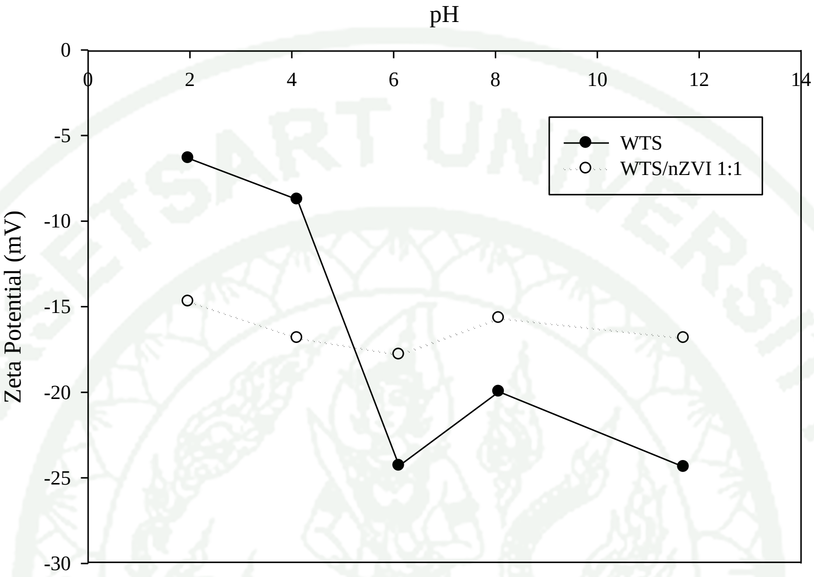

Figure 15 Zeta potential of bare WTS and WTS/nZVI composite 1:1 weight by weight in several pH

Table 6 Zeta potential of bare WTS and WTS/nZVI composite 1:1 weight by weight in several pH

pH	Zeta Potential (mV)							
	Bare WTS				WTS/nZVI 1:1			
	1	2	3	average	1	2	3	average
1.97	-5.43	-7.66	-5.91	-6.33	-15.00	-14.20	-14.90	-14.70
4.11	-8.18	-9.23	-8.83	-8.75	-15.90	-17.30	-17.30	-16.83
6.11	-22.70	-24.10	-26.1	-24.30	-16.40	-17.20	-19.80	-17.80
8.07	-20.30	-19.60	-20.0	-19.97	-14.70	-14.90	-17.40	-15.67
11.70	-23.50	-23.20	-26.4	-24.37	-17.20	-16.90	-16.40	-16.83

1.3 X-ray Diffraction (XRD)

Figure 16 showed the X-ray Diffraction (XRD) pattern of bare WTS compared with WTS/nZVI composite 1:1 weight by weight. The XRD pattern of WTS, there was a high major peak of quartz (SiO_2). The two-theta value was 26.8125. The XRD pattern of WTS/nZVI 1:1, the peak of quartz decreased from intensity 5547 to 805 significantly and there was the peak of nZVI (Fe_0) occurred. The two-theta was 45.034.

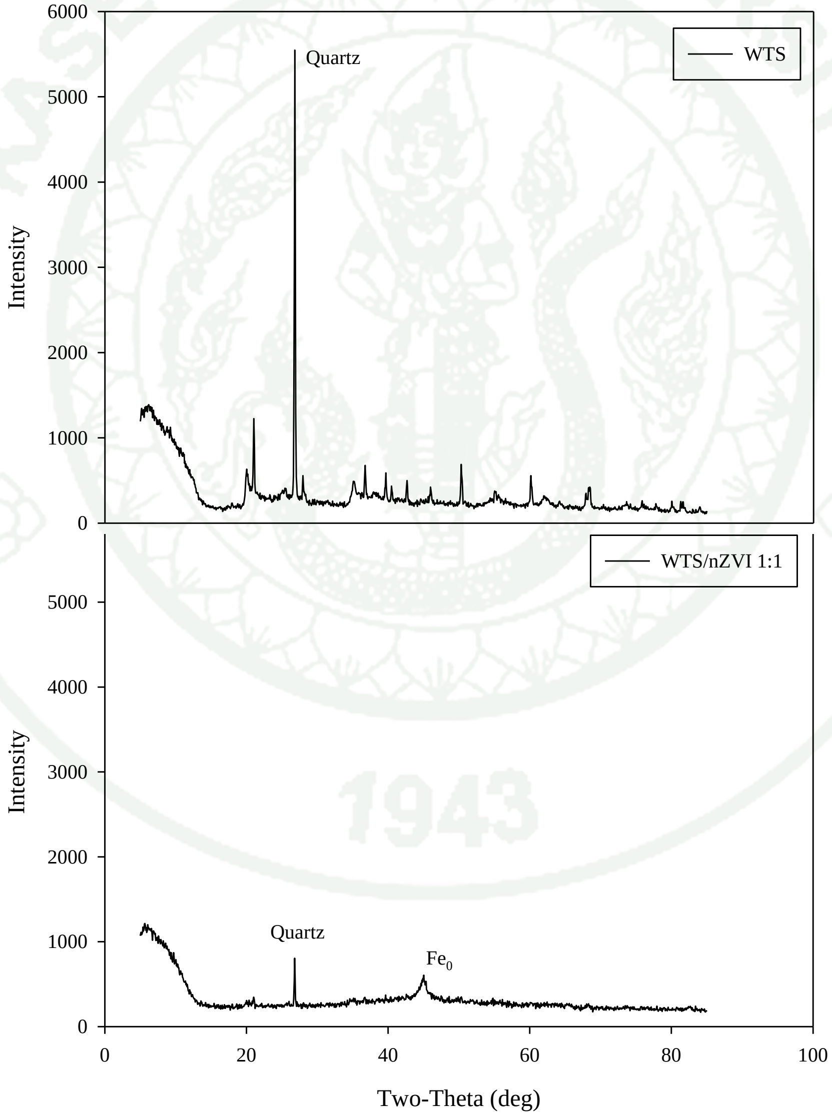

Figure 16 XRD pattern comparison between WTS and WTS/nZVI composite

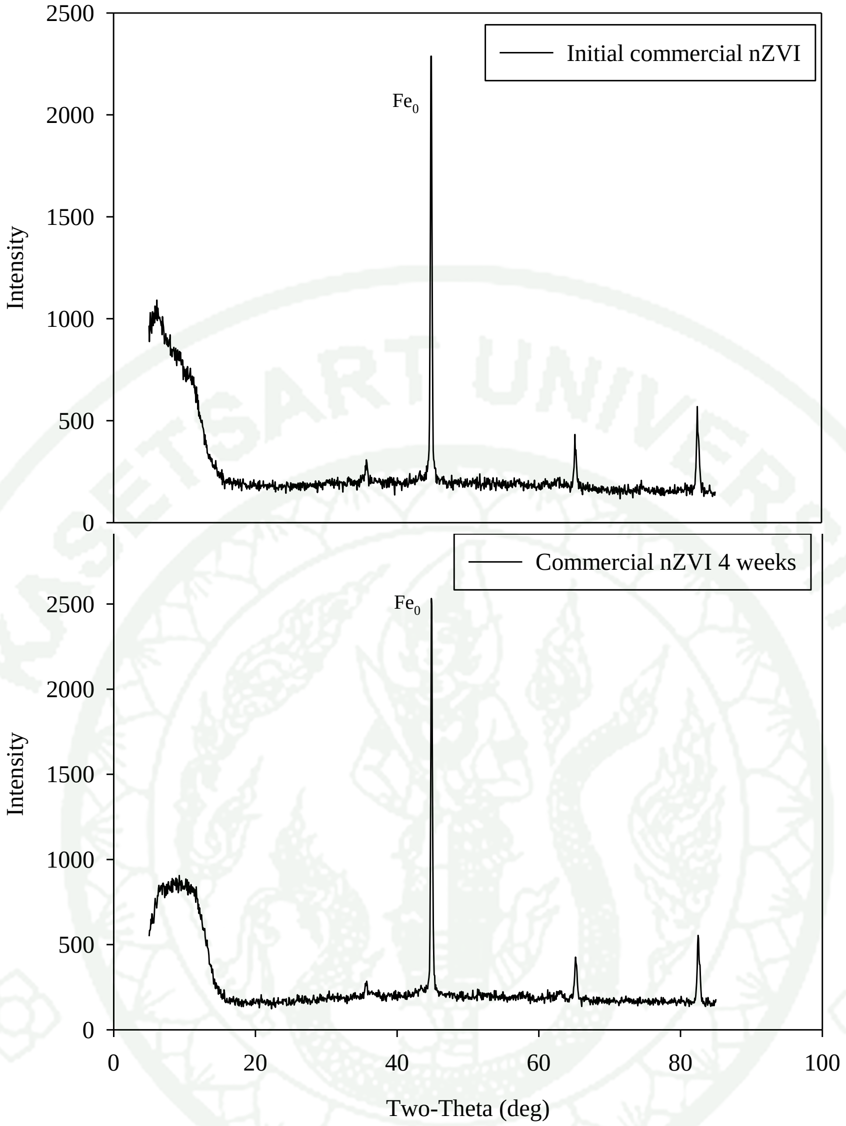

Figure 17 XRD pattern comparison between initial commercial nZVI and 4 weeks passed commercial nZVI after contacting with air

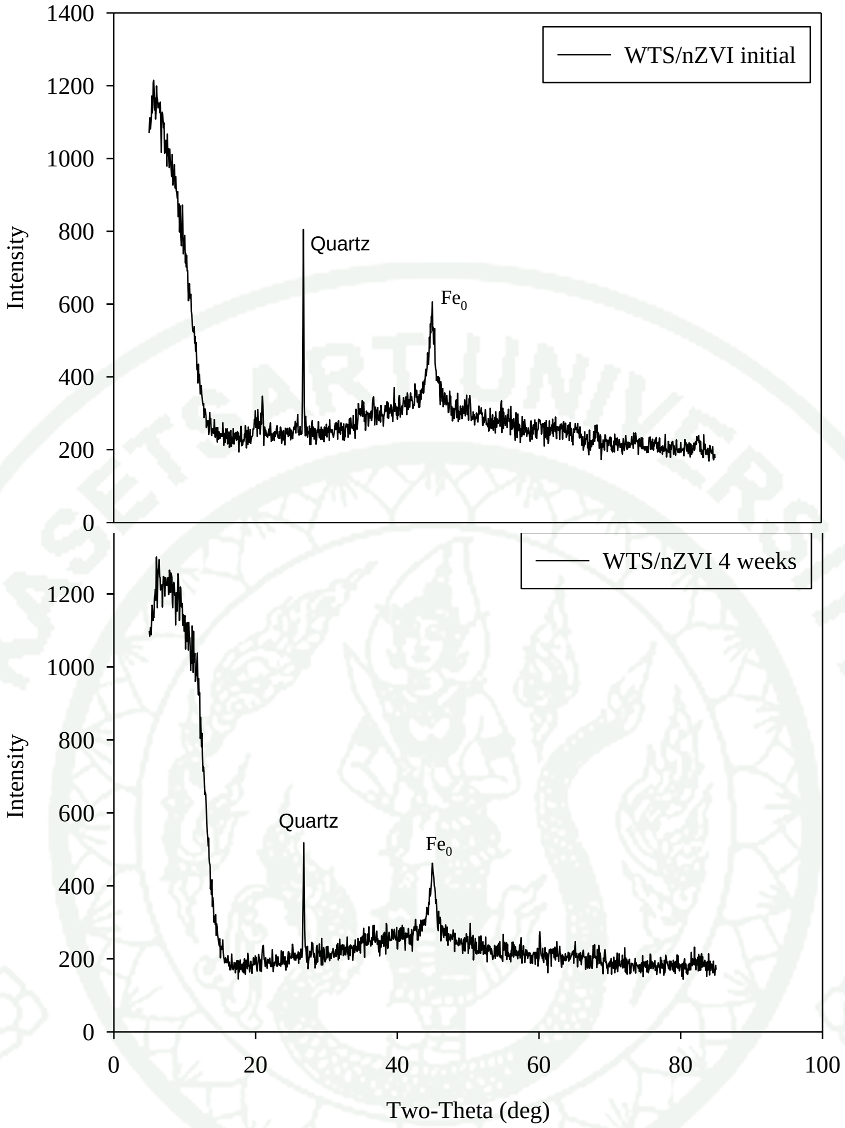

Figure 18 XRD pattern comparison between initial WTS/nZVI composite and 4 weeks passed WTS/nZVI composite 1:1 weight by weight after contacting with air

Figure 17 and 18 showed a stability of commercial nZVI and WTS/nZVI composite 1:1 weight by weight , respectively, when contacted with an air (O_2). Actually nZVI can be oxidized by oxygen (O_2) and a humidity (H_2O) in an air became ferric(III) oxide monohydrate ($Fe_2O_3 \cdot H_2O$). Then a quality of nZVI to remove the heavy metal was decreased. There was a comparison between commercial nZVI contacted with an air 0 and 30 days and WTS/nZVI contacted with an air 0 and 30 days. The results indicated that XRD pattern of initial commercial nZVI had the peak of nZVI at the intensity of 2288 and became 2532 when 30 days passed. The XRD pattern of the initial WTS/nZVI 1:1 had the nZVI peak of 606 and became 462 at 30 days passed. The results implied that there was no significant difference of the intensity of nZVI in both commercial nZVI and WTS/nZVI 1:1 between the initial ones and the 30 days passed ones . Thus, the quality of nZVI of both materials was still the same.

1.4 BET Surface Area

The BET surface area of the materials was considered to measure a surface area value and a total pore volume value (Table 7). After the nZVI addition at the surface of the bare WTS, the surface area value was higher because the small particle of nZVI was attached at the surface of WTS (according to the SEM images). Hence, the total volume was increased from 0.1428 to 0.2916. It implied that WTS/nZVI is able to contact and adsorb more than WTS.

Table 7 BET surface area and total pore volume of WTS and WTS/nZVI composite 1:1 weight by weight

Materials	**BET surface area (m^2/g)**	**Total pore volume (mL/g)**
WTS	39.66	0.1428
WTS/nZVI 1:1	69.03	0.2916

2. Heavy metals removal

2.1 Hexavalent chromium removal

2.1.1 Scanning Electron Microscopes-Energy Dispersive X-ray (SEM-EDX)

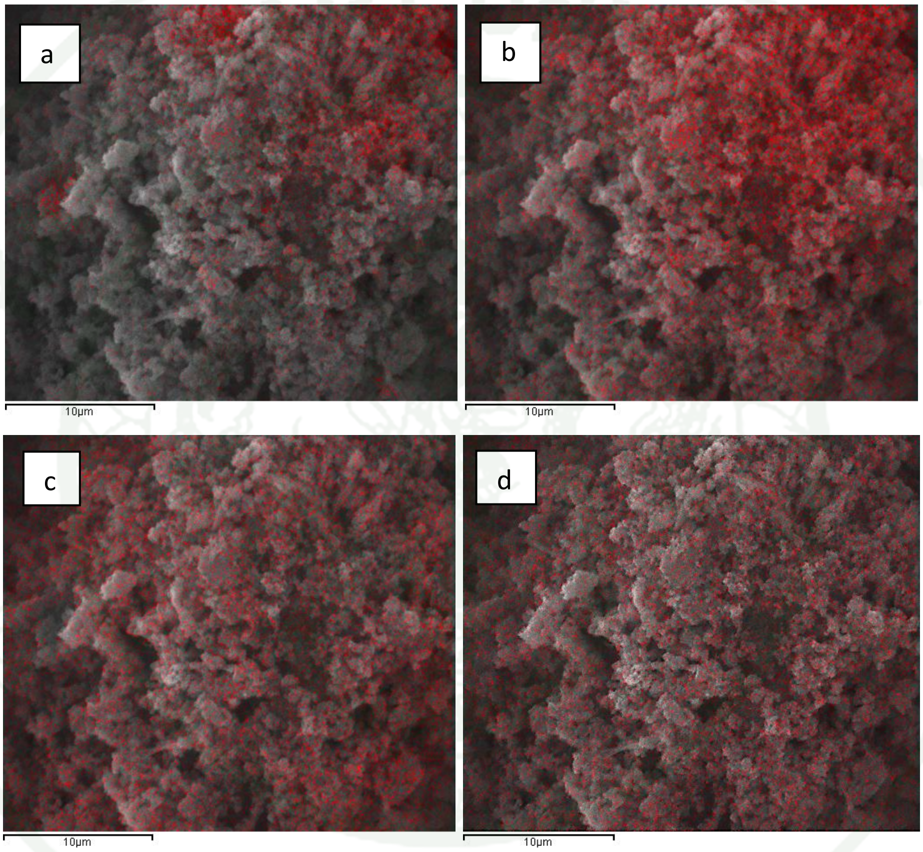

Figure 19 SEM-EDX (500x) of WTS/nZVI after treating with hexavalent chromium when; a) silicon (Si) b) aluminium (Al) c) iron (Fe) d) chromium (Cr)

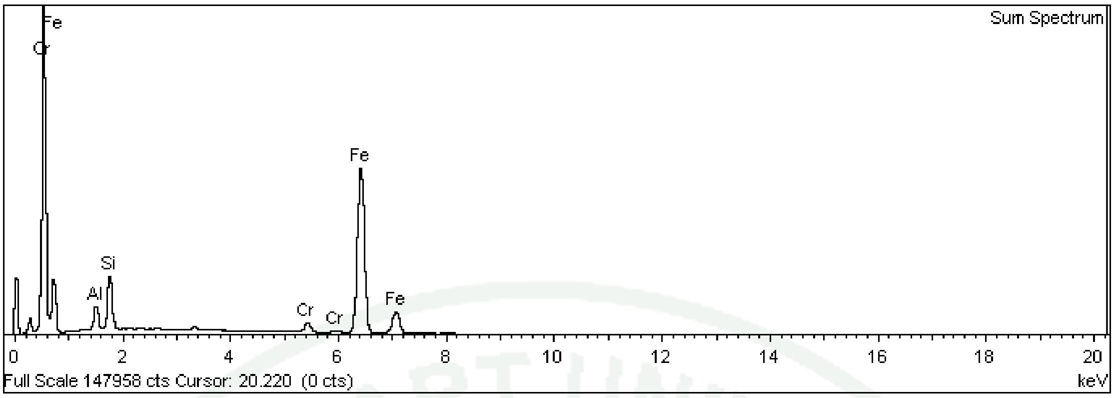

Figure 20 SEM-EDX element quantitative graph

Silicon (Figure 19a) and aluminum (Figure 19b) were the main component of water treatment sludge (WTS). Figure 19c displayed iron which was stand for nZVI. According to Figure 14c, it indicated that nZVI, which was added, was dispersed on the surface of WTS. After Cr(VI) removal, chromium (Figure 19d) was dispersed around the surface of WTS. Chromium settling ($Cr_xFe_{1-x}(OH)_3$) was attached at the surface of WTS dispersedly . WTS/nZVI was not only reducing agent, but also was a supporter for settlings. In addition, Figure 20 showed an amount of element on WTS/nZVI composite surface at one spot of SEM-EDX. An amount of iron was the highest and an amoumt of aluminium was the lowest in analyzed area.

2.1.2 Effect of WTS/nZVI composite ratio

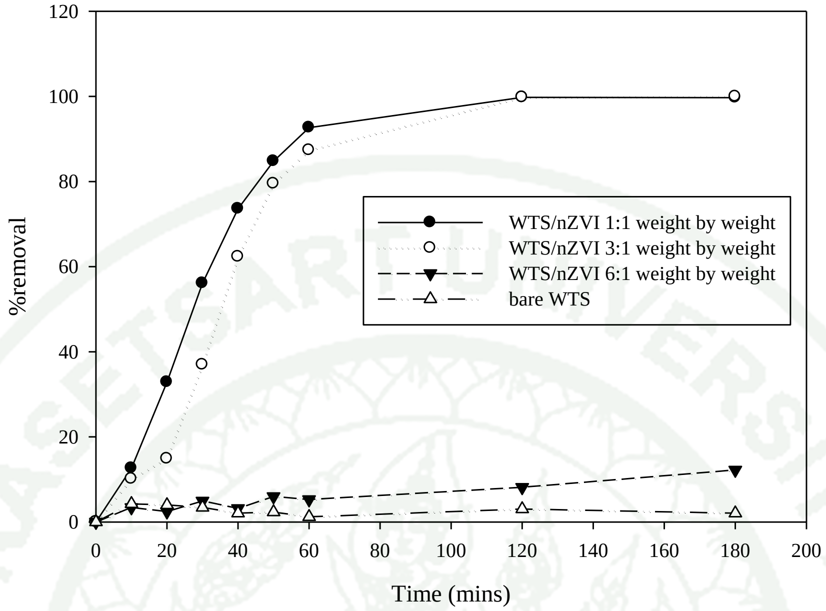

Figure 21 Cr(VI) removal varied the ratio of the composites at 10 mg/L

The result of WTS/nZVI composites ratio variation was presented in Figure 21. The 10 mg/L Cr(VI) was used in the experiment and the pH of the Cr(VI) solution was 5.8. The composite 1:1 (nZVI 0.5 g/g WTS/nZVI composite) can remove Cr(VI) for 99% as same as the composite 3:1 (nZVI 0.33 g/g WTS/nZVI composite), but the composite 1:1 exhibited the faster rate. On the other hands, the composites 6:1 (nZVI 0.167 g/g WTS/nZVI) and WTS took a longer time to remove Cr(VI) in less quantity. The efficacy of Cr(VI) removal of the composite depended on an amount of nZVI in the composites. Increasing of NZVI loading resulted in higher removal efficiency.

Similar to the research of Fu *et al.* (2014) in using of resin supported nZVI in order to remove Cr(VI), there was an experiment that varied an amount of nZVI in the same amount of resin. The result indicated that nZVI load 43.1 mg/g resin-nZVI can remove Cr(VI) 88.1% more than 30.8 mg/g resin-nZVI which can remove Cr(VI) 56.2%. Resin did a role as a carrier of nZVI and its dispersant. Cr(VI) removal efficiency depended on the active sites of nZVI in resin-nZVI.

The main mechanism of nZVI in order to remove Cr(VI) was reduction. Cr(VI) was reduced into Cr(III) that was shown in equation 18-20. Hence, the main mechanism of WTS/nZVI composite to Cr(VI) was also reduction reaction and WTS acted as a dispersant (Fu *et al.*, 2014)

$$2HCrO_4^- + 3Fe^0 + 14H^+ \rightarrow 3Fe^{2+} + 2Cr^{3+} + 8H_2O \quad (18)$$

$$2HCrO_4^- + Fe^0 + 7H^+ \rightarrow Fe^{3+} + Cr^{3+} + 4H_2O \quad (19)$$

$$2CrO_4^{2-} + 3Fe^0 + 16H^+ \rightarrow 3Fe^{2+} + 2Cr^{3+} + 8H_2O \quad (20)$$

2.1.3 Effect of the materials

WTS/nZVI 1:1 weight by weight was chosen for Cr(VI) removal experiment. Three materials were used for 80 mg/L Cr(VI); WTS, commercial nZVI, and WTS/nZVI composite. The results as shown I figure 22 indicated that WTS/nZVI composite can remove Cr(VI) 40% in 360 mins (6 hours). On the other hands, WTS and commercial nZVI can remove Cr(VI) not more than 5% in 6 hours. According to zeta potential result, it indicated that WTS cannot adsorb Cr(VI) because the charges on the surface of WTS and Cr(VI) (CrO_4^{2-}) were both negative charges. In the case of commercial nZVI, the nZVI particles were too dense. Then Cr(VI) cannot be removed effectively. Hence, nZVI particles were put on the surface of WTS in order to disperse the nZVI particles. Cr(VI) was removed effectively. The results conformed with Lv *et al.* (2012) which had studied about Cr(VI) removal using nZVI-Fe_3O_4 nanocomposites. The results indicated that 0.05 g nZVI/g nZVI-Fe_3O_4 can remove Cr(VI) for 96.4%. However, commercial nZVI can remove Cr(VI) only 18.8%. It was because of the aggregation of nZVI.

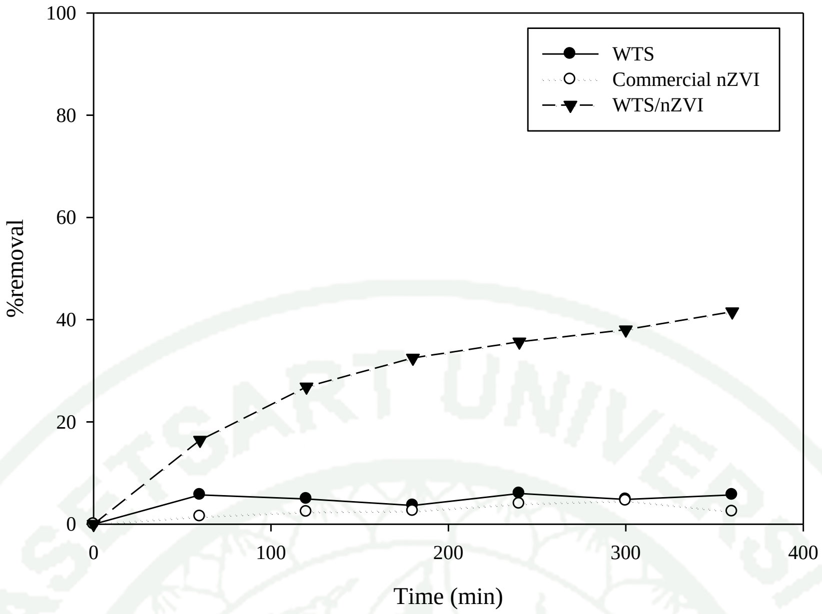

Figure 22 80 mg/L Cr(VI) removal at initial pH 5.8 varied material

2.1.4 Effect of initial concentration

The effect of concentration variation was shown in Figure 22. The WTS/nZVI 1:1 was used in this experiment comparing with bare WTS. The bare WTS had a small adsorption in all concentration of Cr(VI) (Figure 23a.). Comparing with bare WTS (Figure 23b), the WTS/NZVI composite 1:1 removed 10 and 20 mg/L of Cr(VI) up to 99% within 2 hours and remove 40, 60 mg/L, 80 mg/L of Cr(VI) up to 95%, 66%, and 44% with 10 hours, respectively. According to the previous research, Liu *et al.* (2014) had studied about Cr(VI) and Hg(II) removal using pumice supported nZVI (P-nZVI). The results indicated that P-nZVI can remove 40 and 60 mg/L Cr(VI) 99.8%. However it can remove 100 mg/l Cr(VI) 85.8%. Hence, when the Cr(VI) initial concentration increased, the Cr(VI) removal efficacy decreased, but an amount of Cr(VI) reacted in one area of active site increased.

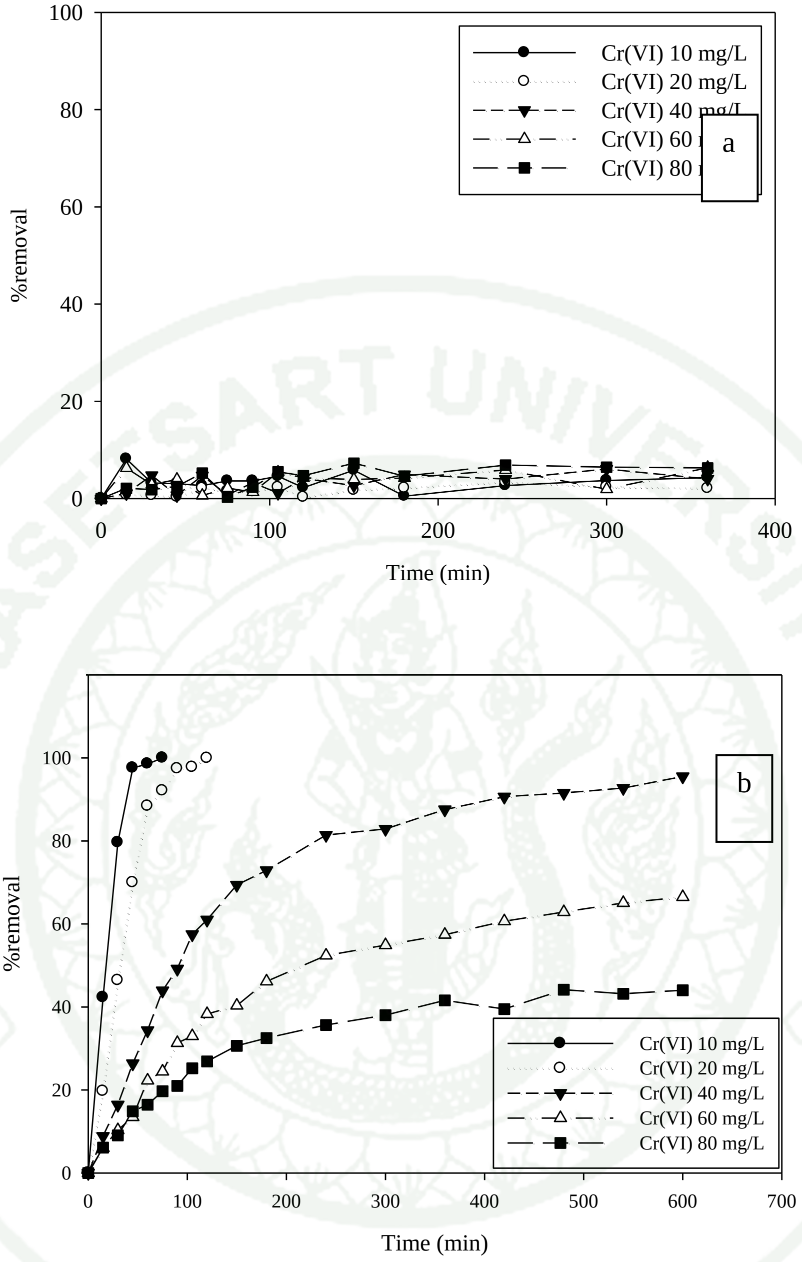

Figure 23 Cr(VI) initial concentration effect in Cr(VI) removal of a) WTS and b) WTS/nZVI

2.1.5 Effect of initial pH

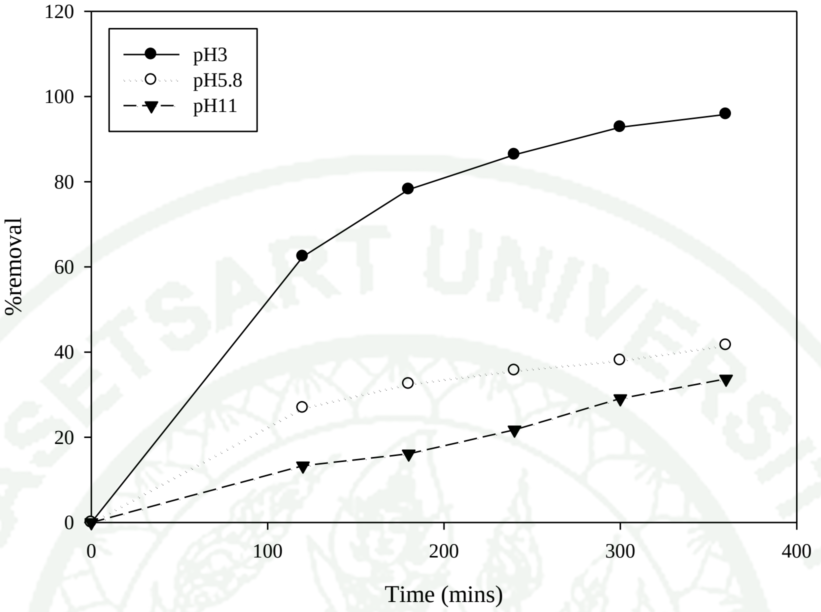

Figure 24 Cr(VI) initial pH effect in Cr(VI) removal of WTS/nZVI composite

Initial pH of the Cr(VI) solution was a significant factor which affects Cr(VI) removal. It affected the charges at the surface of the material and Cr(VI) ions in the solution. Cr(VI) solution at pH1, Cr(VI) ions is a chromic acid form (H_2CrO_4). Cr(VI) solution at pH2-pH7, Cr(VI) ions are hydrogendichromate ion form ($HCrO_4^-$). Cr(VI) solution at pH8 and higher, Cr(VI) ion are chromate ion form (CrO_4^{2-}) (Lv *et al.*, 2012).

A 80 mg/L of Chromium (VI) removal at pH3, 5.8, and 11 was studied in order to find the best initial pH of Cr(VI) solution appropriated for Cr(VI) removal. The result indicated that the maximum Cr(VI) removal was pH3 Cr(VI) solution. The removal efficiency was up to 97.9% (Figure 24). Thus, Cr(VI) can be removed effectively at low pH. According to equation 19-21, nZVI needed H^+ in order to reduce Cr(VI). In case that there were more H^+ in the solution, Cr(VI) removal increase. Thus, if the solution was in an acid condition, the Cr(VI) was strongly reduced to Cr (III) and if the solution was in an alkaline condition, the Cr(VI) was weakly reduced to Cr(III). According to the previous research, Fu *et al.* (2013)

studied about Cr(VI) removal using resin supported nZVI (R-nZVI). The results indicated that R-nZVI can remove Cr(VI) 95.6% at pH3 and can remove Cr(VI) 88.4%, 45.4%, and 37.9% at pH 5, 7, and 9, respectively. Not only H^+, OH^- also participated in Cr(VI) removal. At higher pH value, Cr(III) and Fe(III) ions attached with OH^- and obstructed at the nZVI surface. Hence, the Cr(VI) removal efficiency increase when pH values decrease (Lv *et al.*, 2012).

2,2 Trivalent Chromium Removal

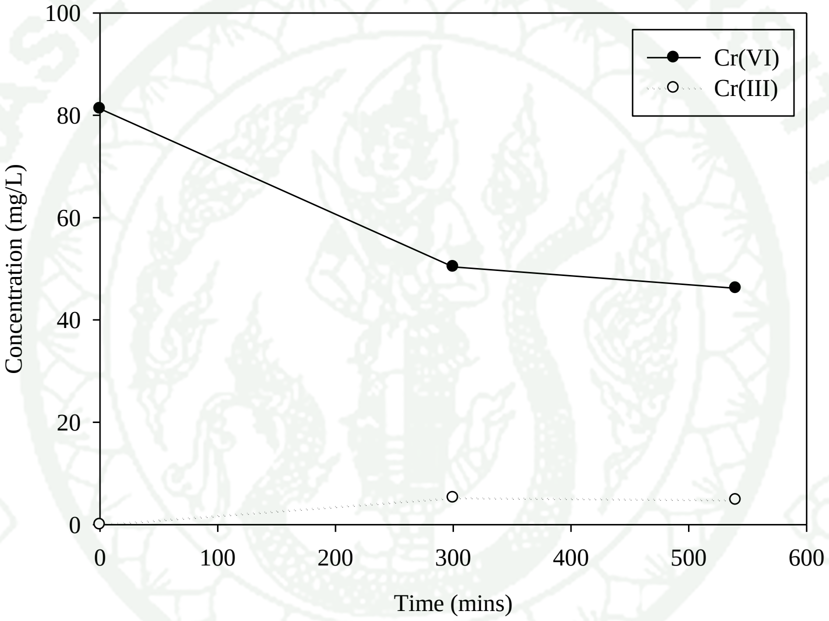

Figure 25 Cr(VI) and Cr(III) removal at initial concentration 80 mg/L

Figure 25 showed Cr(VI) and Cr(III) removal of WTS/nZVI. It can remove 80 mg/L, pH5.8 Cr(VI) to 50 mg/L within 9 hours. However, there was Cr(III) remained in the solution. Cr(III) was reduced from Cr(VI) by nZVI. There was 5 mg/L Cr(III) remained in the solution. Cr(III) can be removed from the solution by precipitating in $Cr_xFe_{1-x}(OH)_3$ form as equation 21 and being adsorbed by WTS/nZVI (Fu *et al.*, 2013).

$$(1-x)Fe^{3+} + xCr^{3+} + H_2O \rightarrow Cr_xFe_{1-x}(OH)_3\downarrow + 3H^+ \qquad (21)$$

2.3 Residual Iron

According to equation 21, Fe(III) from nZVI occurred when Cr(VI) was reduced into Cr(III). The residual iron concentration was detected by FAAS. Table 8 showed residual iron (Fe) concentration in 10 and 80 mg/L Cr(VI) solution. The samples were collected until the solution was in equilibrium condition. All values were between 0.001-0.009 mg/L excepted in the initial 10 mg/L Cr(VI) solution. It increased from 0.005 to 0.028 mg/L. Cr(VI) was completely reduced by WTS/nZVI composite 1:1 within 45 minutes. After that, there were not Cr(VI) ions in the solution. nZVI was oxidized by H_2O instead and occurred Fe(II) and Fe(III) ions in the solution. Figure 26 showed an amount of residual iron in 10 and 80 mg/L Cr(VI) solution. It indicated that an iron concentration in the solution was nearly zero. The occurred Fe(III) can co-precipitate with Cr(III) and form $Cr_xFe_{1-x}(OH)_3\downarrow+3H^+$ precipitated.

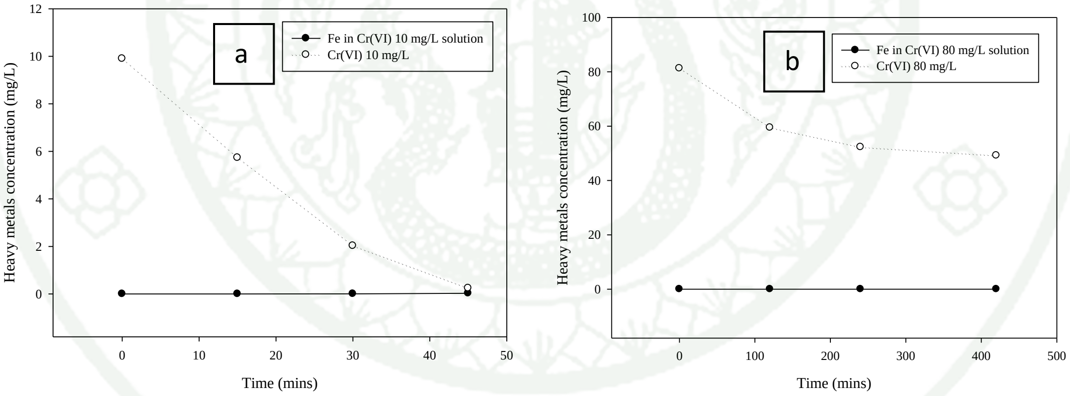

Figure 26 Fe residual of Cr(VI) at initial concentration a) 10 g/L b) 80 mg/L

Table 8 Residual Fe in both initial Cr(VI) 10 and 80 mg/L

Initial Cr(VI) 10 mg/L		**Initial Cr(VI) 80 mg/L**	
Time (min)	**Residual Fe Conc.**	**Time (min)**	**Residual Fe Conc.**
0	0.001	0	0.001
15	0.001	120	0.009
30	0.005	240	0.003
45	0.028	420	0.003

2.4 Lead removal

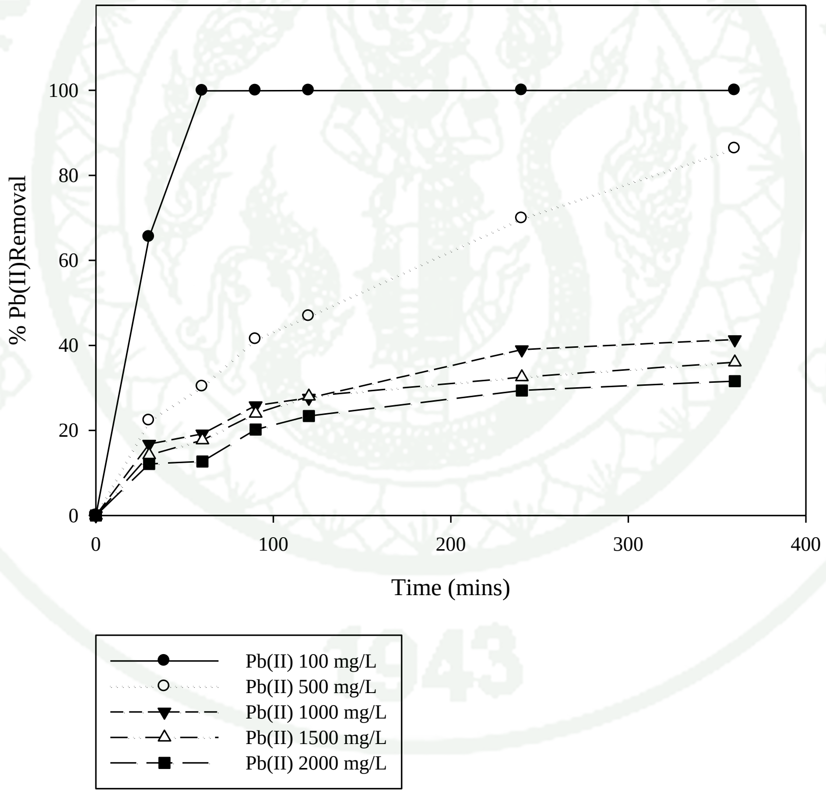

Figure 27 Pb(II) removal varied initial concentration

The results of Pb(II) removal of WTS/nZVI composite by varying initial Pb(II) concentration were illustrated in Figure 27. WTS/nZVI can remove 100 mg/L Pb(II) 99% within 1 hour and can remove 500 mg/L Pb(II) 86% within 6 hours. On the other hands, WTS/nZVI can remove 1000, 1500, and 2000 mg/L Pb(II) 36%, 41%, 31%, respectively. According to the previous research, Arshadi *et al.* (2014) had studied about nZVI supported sineguelas waste (S-NaOH-nZVI) for Pb(II) removal. The results indicated that S-NaOH-nZVI can removed 30 and 1000 mg/L Pb(II) for 97.6% and 22.5%, respectively. Hence, in case that the initial concentration of Pb(II) increased, the efficiency of Pb(II) removal decreased because of Pb(II) ions increase at the limited of the active site of nZVI. In addition, the mechanism of Pb(II) removal was Fe-Pb redox reaction. The rapid reaction of Pb(II) to Pb_0 on the surface of the WTS/nZVI composite occurred simultaneously with the oxidation of Fe_0 to Fe(II). The reaction was shown below as equation 22 (Arshadi *et al*., 2014).

$$Pb^{2+} + Fe_0 \quad \leftrightarrow \quad Pb_0 + Fe^{2+} \tag{22}$$

3. Langmuir-Hinshelwood-Hougen-Watson kinetics

According to the plots of LHHW linear graph of Cr(VI) (Figure 28a) and the calculation, the R^2 was 0.934, k_r mg/L-min was 0.510 and K_{ads} was 0.028 L/mg. It indicated that the reduction reaction at the surface of composite affected the Cr(VI) reduction more than adsorbed at the surface. However, there was still the adsorption process involved because K_{ads} value was more than 0.001. $Cr_xFe_{1-x}(OH)_3$ sediments were adsorbed by WTS which was a sediment support and dispersant. In case of Pb(II), the LHHW linear graph was shown in Figure 28b. According to the calculation, the R^2 was 0.999, k_r was 21.459 mg/L-min and K_{ads} was 0.0006 L/mg. It meant that the major mechanism to remove Pb(II) was reduction reaction and adsorption didn’t involve in the process because K_{ads} value was in a very small amount even if the bare sludge can adsorb the Pb(II) ions.

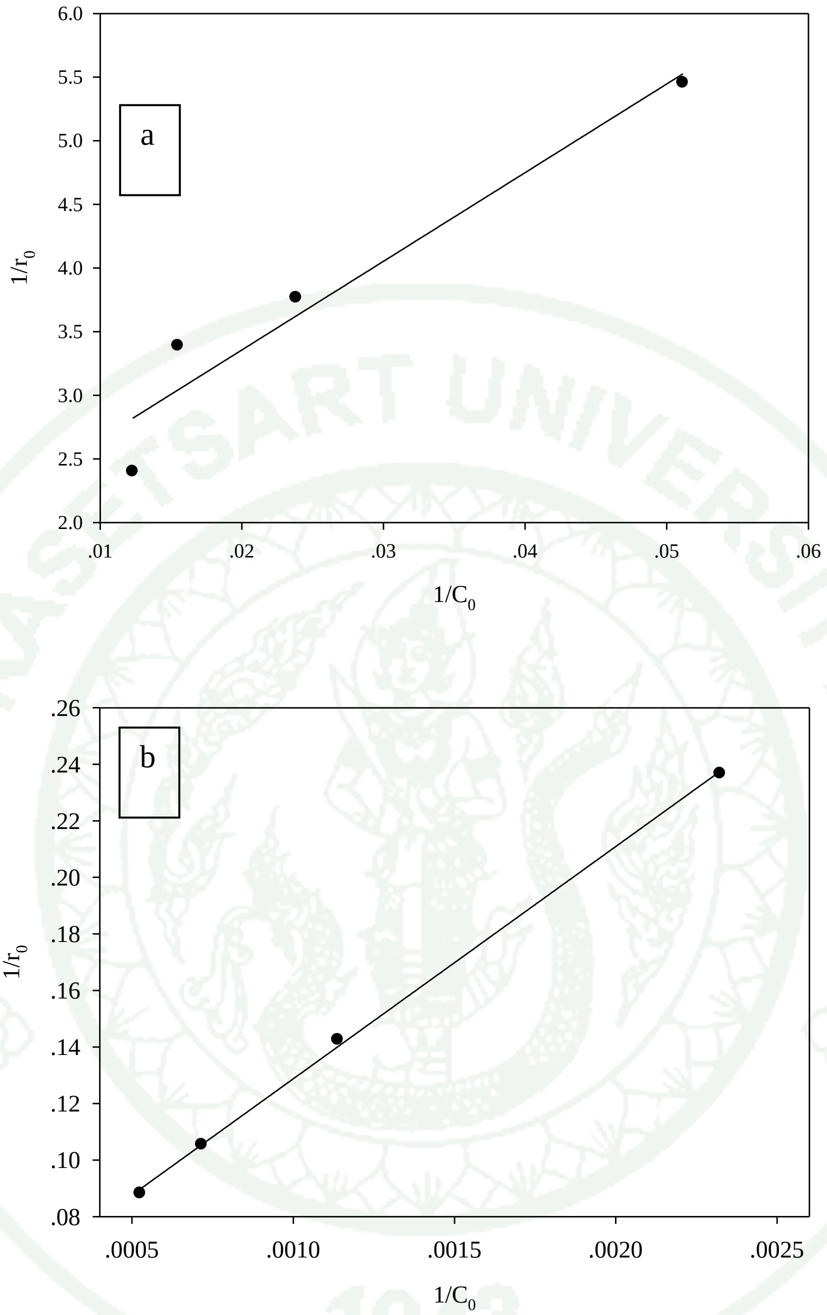

Figure 28 Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics of a) Cr(VI) removal, b) Pb(II)

The efficiency of pollutants removal is described by reaction rate constant (k_r) and adsorption equilibrium constant (K_{ads}). Table 9 showed the comparison of k_r and K_{ads} between WTS/nZVI composite 1:1 weight by weight and others materials in Cr(VI) removal and other pollutants. Naimi-Joubani *et al.* (2014) studied about photocatalytic reduction Cr(VI) with illuminated ZnO/TiO2 composite. The method of Cr(VI) removal of this study was photocatalytic reduction. The illuminated ZnO/TiO2 composite can remove 20 mg/L Cr(VI) for 99% within 2 hours. The k_r and K_{ads} values were 0.4240 mg/L-min and 0.0430 L/mg, respectively. Comparing with WTS/nZVI composite 1:1, it can remove 20 mg/L Cr(VI) for 99% within 2 hours and the k_r and K_{ads} values were 0.5097 mg/L-min and 0.0282 L/mg. It can describe that the Cr(VI) removal efficiency of the illuminated ZnO/TiO_2 composite and WTS/nZVI composite 1:1 were not different significantly. Moreover, there were the use of nZVI in order to remove other pollution using LHHW kinetics. The results in table 7 revealed the comparison of k_r and K_{ads} values. Other than Cr(VI), WTS/nZVI composite 1:1 can remove Pb(II) which had k_r and K_{ads} values for 21.459 mg/L-min and 0.0006 L/mg, respectively. The nZVI in other studies had k_r value less than WTS/nZVI composite's. Considering from k_r and K_{ads} value, the nZVI composite was appropriate to remove heavy metals by the reaction mechanism. On the other hands, organic substances were appropriate to be removed by nZVI composite with adsorption mechanism.

Table 9 The Comparison of k_r (mg/L-min) and K_{ads} (L/mg) in the LHHW kinetics

Material	**Pollutant**	**k_r**	**K_{ads}**	**R^2**	**Reference**
WTS/nZVI	Cr(VI)	0.5097	0.0282	0.934	This work
WTS/nZVI	Pb(II)	21.459	0.0006	0.999	This work
Illuminated ZnO/TiO2 composite	Cr(VI)	0.4240	0.0430	-	Naimi-Joubani et al., 2014
Zero Valent Iron (ZVI) with UV light	1,4-dioxane	0.0320	0.1060	0.818	Son et al., 2009
nZVI	Pentachrolophenol	0.1980	8.8200	0.965	Li et al., 2011
nZVI suppported with organobentonite	Atrazine	0.0548	2.8000	0.998	Zhang et al., 2012

4. Langmuir and Freundlich Isotherm

According to the results of LHHW kinetics, Cr(VI) removal using WTS/nZVI composite 1:1 had adsorption involved. Hence, Langmuir and Freundlich isotherm was used to describe the adsorption mechanism and the interaction between adsorbate and adsorbent. Figure 29 represented the Langmuir and Freundlich isotherm of Cr(VI) in linear, respectively. It indicated that the adsorption pattern suited with the Langmuir isotherm better than Freundlich isotherm because of the R^2 value. Thus, $Cr_xFe_{1-x}(OH)_3$ particles adsorbed on WTS surface by only monolayer adsorption . The constant related to the adsorption capacity (K_L) was 0.952 L/mg and the maximum adsorption capacity (q_{max}) was 63.29 mg/g. The K_L value was less than the powder activated carbon's (1.022 L/mg), but the q_{max} value was more (Table 10). Thus, WTS/nZVI had higher efficiency than the powder activated carbon to remove Cr(VI). The K_L value of WTS/nZVI 1:1 was low compared with other adsorbent because the main mechanism of chromium removal wasn't adsorption (considering from LHHW kinetics). On the other hands, the q_{max} value was high. It was affected by the reaction mechanism of nZVI to remove Cr(VI). Hence, WTS/nZVI has higher ability to remove Cr(VI) than other adsorbent.

Table 10 The Comparison of values and constants in the Langmiur and Freundlich isotherm in Cr(VI) removal

Adsorbent	**Initial pH**	**Langmuir**				**Freundlich**			**Ref**
		q_{max} (mg/g)	**K_L (L/mg)**	**R_L**	**R^2**	**K_F (L/g)**	**n**	**R^2**	
WTS/nZVI 1:1	5.8	63.29	0.952	0.096	0.998	23.10	2.428	0.872	This work
Powder activated carbon	4.0	46.90	1.022	0.661	0.998	13.30	1.583	0.971	Jung *et al.*, 2014
Chitosan	4.0	35.60	1.149	0.635	0.999	8.25	2.050	0.906	Jung *et al.*, 2014
nZVI-Fe3O4	8.0	29.43	6.210	-	0.997	14.15	6.170	0.999	Lv *et al.*, 2012

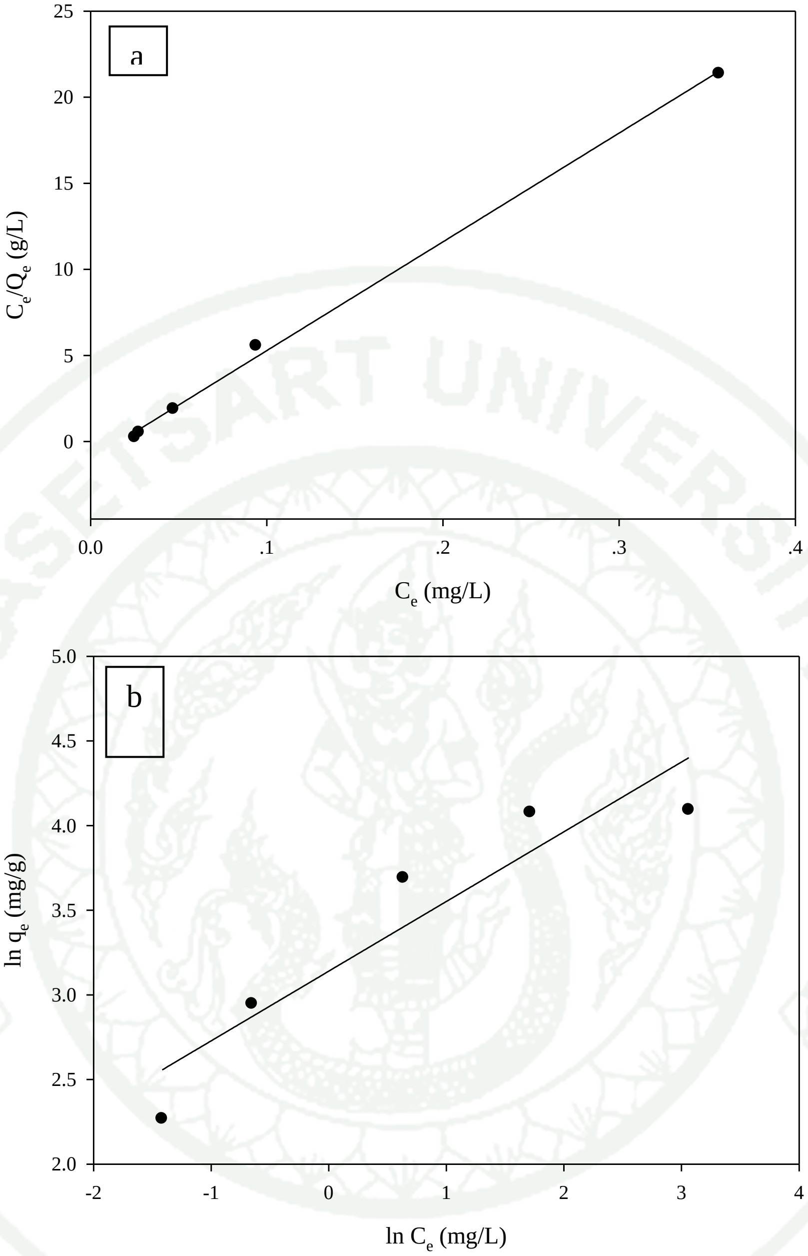

Figure 29 Adsorption Isotherm of Cr(VI) removal; Langmuir (a) and Freundlich (b) of Cr(VI) removal

5. Pseudo-first order kinetics and pseudo-second order kinetics

According to the table 11 and 12 and the figure 30 and 31, it showed the experiment data fit of the pseudo second-order kinetics model for different initial concentration of Cr(VI) and pH removed by WTS/nZVI composite. It was found that correlation coefficient values of first-order kinetic model were lower than second-order kinetic model. It indicated the bad quality of linearization. In comparison, the second-order kinetic model can be fitted the experimental data better than first-order kinetic model. The linearity showed that this model can be applied to predict the kinetics of this reaction. The results demonstrated a decrease in k_2 values from 0.992 to 0.00004 g/mg-min and an increase q_e from 9.89 to 62.50 mg/g when initial concentration increased from 10 to 80 mg/L.

Table 11 Pseudo first order kinetics of Cr(VI) removal varied initial Cr(VI) concentration

Initial Cr(VI) conc.	**Pseudo-first order**			
	q_e exp (mg/g)	**q_e cal (mg/g)**	**k_1 (min^{-1})**	**R^2**
10mg/L	9.8950	6.6819	0.0709	0.9416
20mg/L	19.5339	36.4083	0.0668	0.9326
40mg/L	41.8681	24.0991	0.0039	0.9933
60mg/L	64.3021	39.9117	0.0007	0.8993
80mg/L	59.9057	39.8841	0.0007	0.9291

Table 12 Pseudo second order kinetics of Cr(VI) removal varied initial Cr(VI) concentration

Initial Cr(VI) conc.	**Pseudo-second order**			
	q_e exp (mg/g)	**q_e cal (mg/g)**	**k_2 (g/mg-min)**	**R^2**
10mg/L	9.8950	9.8912	0.992350	1.0000
20mg/L	19.5339	19.5313	0.054274	1.0000
40mg/L	41.8681	42.7350	0.000365	0.9997
60mg/L	64.3021	66.6667	0.000053	0.9966
80mg/L	59.9057	62.5000	0.000048	0.9940

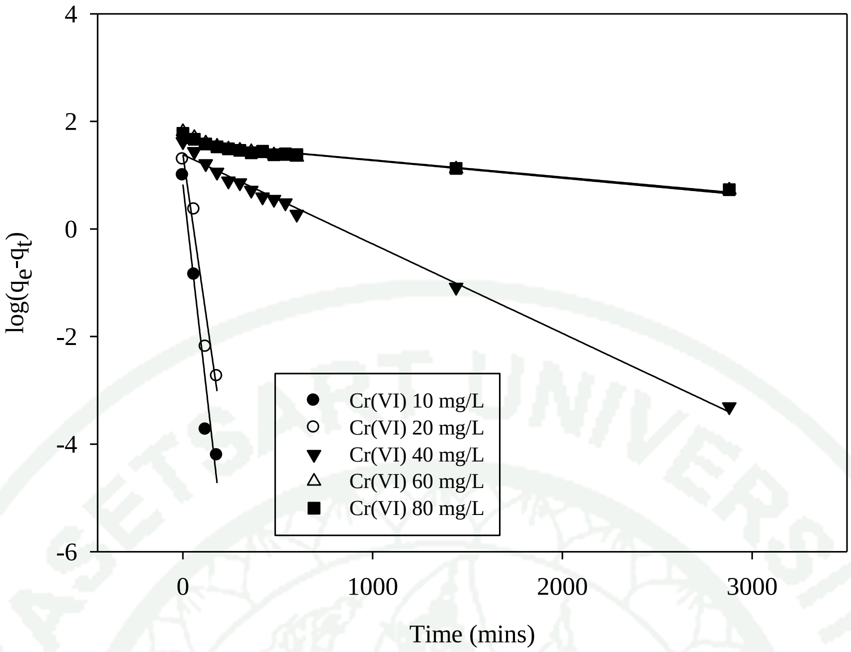

Figure 30 Pseudo first-order kinetics of Cr(VI) removal of WTS/nZVI composite

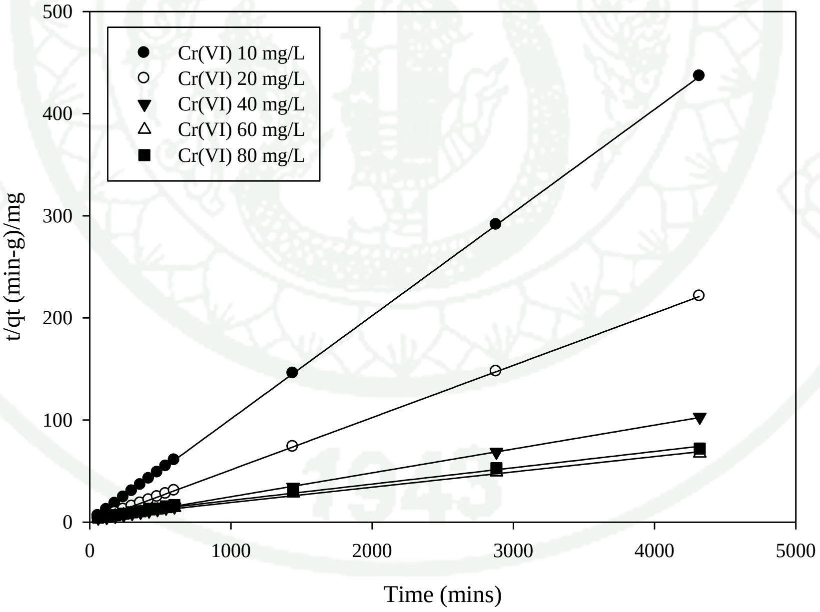

Figure 31 Pseudo second-order kinetics of Cr(VI) removal of WTS/nZVI composite

6. Total Cr from Electroplating wastewater treatment

The wastewater, which was used in the experiment, was from rinsing process. It was 360 mg/L of initial Cr and had initial pH at 1. Hence, there was pH adjustment into pH3 according to initial the previous pH experiment. The WTS/nZVI composite used at rate 1g/L as a powder form. The result indicated that total Cr was removed from wastewater up to 99% within 14 hours (Figure 32). pH value of the solution raised because Cr(VI) reduction needed H^+. The final pH was at 5.

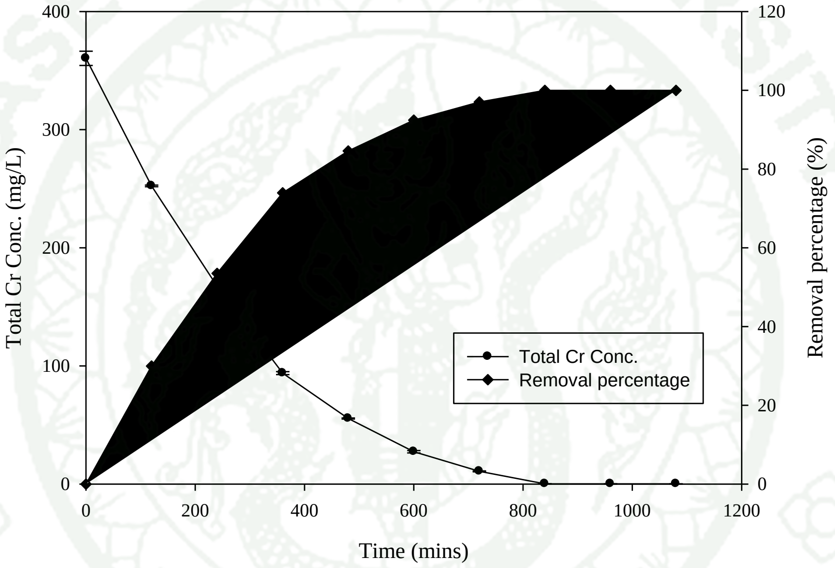

Figure 32 Total Cr concentration residual and total Cr removal percentage of WTS/nZVI composite for electroplating wastewater

CONCLUSIONS AND RECOMENDATIONS

Conclusions

The optimal ratio of water treatment sludge/nano zero valent iron (WTS/nZVI) composite was WTS/nZVI 1:1 weight by weight. It can remove 10 mg/L hexavalent chromium (Cr(VI)) for 99% removal within 45 minutes. In case that WTS/nZVI composite had more amount of nZVI, Cr(VI) was removed more effectively. The main mechanism of Cr(VI) removal was reduction which depended on nZVI. WTS was just a carrier, a dispersant, and a sediment supporter of nZVI.

In case that the initial concentration of Cr(VI) solution was low, Cr(VI) was removed rapidly. The 10 mg/L Cr(VI) can be removed for 99% within 45 minutes by WTS/nZVI composite 1:1. On the other hands, the 80 mg/L Cr(VI) had the most of Cr(VI) ions per surface area. Moreover, bare WTS can removed low amount of Cr(VI). The appropriate initial pH of Cr(VI) solution was pH3. Cr(VI) can be removed rapidly which can remove 80 mg/L Cr(VI) for 99% within 6 hours. H^+ was needed for Cr(VI) reduction reaction. In case that initial pH was low, there were a lot of H^+. After the 80 mg/L Cr(VI) removal process had performed for 9 hours, there were Cr(III) occurred 5.24 mg/L and there were total Fe occurred 0.003mg/L since Cr(III) and Fe(III) can react and precipitate to $Cr_xFe_{1-x}(OH)_3$ form. The sediment can be supported by WTS.

WTS/nZVI composite can remove Pb(II). The 100 mg/L Pb(II) can be removed for 99% within an hours by WTS/nZVI composite 1:1 weight by weight which was the fastest performance.

Considering from R^2 and k_r, the Pb(II) removal model was fitted for Langmuir-Hinshelwood-Heugen-Watson Kinetics more than Cr(VI) removal and WTS/nZVI composite can remove Pb(II) more efficient than Cr(VI). In case of Cr, k_r was 0.51 mg/L-min and K_{ads} was 0.028 L/mg (R^2 = 0.934). It meant that the reduction reaction was the main mechanism in Cr(VI) removal by WTS/nZVI composite, but there was the supportive mechanism which was adsorption ($Cr_xFe_{1-x}(OH)_3$ supported by WTS). In case of Pb(II), k_r was 21.46 mg/L-min and K_{ads} was 0.00057 L/mg (R^2 = 0.999). Thus, reduction reaction was also the main mechanism in Pb(II) removal, but adsorption did not affiliate because of low K_{ads} value. Considering from R^2 and k_r, the Pb(II) removal model was fitted more than Cr(VI) removal and WTS/nZVI composite can remove Pb(II) more efficient than Cr(VI). However, Pb(II) removal process caused a lot of Fe(III) occurred in the solution. Moreover, although Pb(II) was reduced to Pb_0, the sediment of Pb(0) was large and suspended in the solution thoroughly. Hence, in case that considering from the surrounding factors, Cr(VI) was an appropriate heavy metal removed by WTS/nZVI composite. Since Cr(VI) removal process involved adsorption, Langmuir and Freundlich isotherm were used to describe adsorption behavior of WTS/nZVI composite. The results suited with Langmuir isotherm more than Freundlich Isotherm. The q_{max} value was 63.29 mg/g, K_L value was 0.952 L/mg, and R^2 value was 0.998. Thus it was a monolayer adsorption occurred on homogeneous surface ($Cr_xFe_{1-x}(OH)_3$ supported by WTS). The results suited with and pseudo second-order model more than Pseudo first-order model. The R^2 values were more than 0.993. Thus, the rate of the reaction removed Cr(VI) and Fe(III) depended on the concentration of Cr(VI), Pb(II), and Fe_0 whereas in case that the concentration of Cr(VI) and Pb(II) increased, k_2 value decreased.

Chromium rinsing wastewater from electroplating manufacturing were used to test the efficiency of total Cr removal. The initial concentration and pH was 360 mg/L and 1, respectively. The WTS/nZVI composite 1:1 can remove total Cr for 99% within 17 hours.

Recommendations

1. Due to high concentration Cr(VI) and Pb(II) removal took a long time, the dosage of WTS/nZVI composite should be studied . The dose maybe increases in order to reduce the reaction time.

2. Fe-WTS (WTS using $FeCl_3$ as a coagulant) is maybe used instead Al-WTS (WTS using $AlSO_3$ as a coagulant). In WTS/nZVI composite synthesis process, there is no need to add $FeCl_3$ because it exceeds in the material. It is cost reduction.

3. Preventing the oxidation of WTS/nZVI composite and reserving the quality, there should be O_2 purging by N_2 both in rinsing water and the experiment atmosphere.

4. Cr(VI) plating wastewater from electroplating manufacturing should be studied by increasing the dose of WTS/nZVI composite.

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APPENDICES

Appendix A

Raw data

Appendix A: Raw data

Appendix Table A1 A 10 mg/L Cr(VI) removal by WTS/nZVI 1:1 composite from synthetic wastewater

Time (mins)	Absorbance				Cr(VI) conc. (mg/L)		Removal percentage
	1	2	SD	Ave	Diluted conc.	conc.	
0	0.804	0.799	0.003	0.801	0.990	9.898	0.000%
15	0.470	0.458	0.006	0.464	0.573	5.732	42.295%
30	0.175	0.153	0.011	0.164	0.203	2.027	79.595%
45	0.025	0.015	0.005	0.020	0.024	0.243	97.558%
60	0.025	0.014	0.005	0.020	0.024	0.241	97.570%

Appendix Table A2 A 20 mg/L Cr(VI) removal by WTS/nZVI 1:1 composite from synthetic wastewater

Time (mins)	Absorbance				Cr(VI) conc. (mg/L)		Removal percentage
	1	2	SD	Ave	Diluted conc.	conc.	
0	0.790	0.793	0.002	0.792	0.978	19.553	0.000%
15	0.640	0.652	0.006	0.646	0.798	15.954	19.700%
30	0.428	0.434	0.003	0.431	0.533	10.654	46.372%
45	0.235	0.248	0.007	0.242	0.298	5.966	69.970%
60	0.089	0.098	0.004	0.093	0.115	2.306	88.392%
75	0.056	0.071	0.007	0.064	0.079	1.574	92.078%
90	0.014	0.028	0.007	0.021	0.026	0.521	97.379%
105	0.014	0.028	0.007	0.021	0.026	0.521	97.379%
120	0.014	0.028	0.007	0.021	0.026	0.521	97.379%

Appendix Table A3 A 40 mg/L Cr(VI) removal by WTS/nZVI 1:1 composite from synthetic wastewater

Time (mins)	**Absorbance**				**Cr(VI) conc. (mg/L)**		**Removal percentage**
	1	**2**	**SD**	**Ave**	**Diluted conc.**	**conc.**	
0	0.836	0.863	0.014	0.849	1.049	41.961	0.000%
15	0.752	0.797	0.023	0.774	0.956	38.249	8.845%
30	0.696	0.725	0.014	0.710	0.877	35.080	16.397%
45	0.612	0.639	0.014	0.625	0.772	30.894	26.374%
60	0.535	0.581	0.023	0.558	0.689	27.551	34.340%
75	0.464	0.489	0.013	0.476	0.588	23.536	43.908%
90	0.413	0.451	0.019	0.432	0.533	21.329	49.169%
105	0.339	0.384	0.022	0.361	0.446	17.849	57.462%
120	0.290	0.372	0.041	0.331	0.409	16.369	60.991%
150	0.216	0.304	0.044	0.260	0.321	12.853	69.369%
180	0.173	0.288	0.057	0.231	0.285	11.391	72.854%
240	0.107	0.209	0.051	0.158	0.195	7.802	81.407%
300	0.087	0.204	0.059	0.146	0.180	7.191	82.862%
360	0.060	0.152	0.046	0.106	0.131	5.233	87.530%
420	0.037	0.122	0.043	0.080	0.099	3.944	90.602%
480	0.017	0.127	0.055	0.072	0.089	3.555	91.528%
540	0.015	0.108	0.046	0.062	0.076	3.057	92.714%
600	0.007	0.069	0.031	0.038	0.047	1.885	95.507%

Appendix Table A4 A 60 mg/L Cr(VI) removal by WTS/nZVI 1:1 composite from synthetic wastewater

Time (mins)	Absorbance				Cr(VI) conc. (mg/L)		Removal percentage
	1	2	SD	Ave	Diluted conc.	conc.	
0	0.865	0.878	0.007	0.871	1.076	64.568	0.000%
15	0.835	0.803	0.016	0.819	1.011	60.690	6.006%
30	0.792	0.771	0.011	0.781	0.965	57.909	10.313%
45	0.780	0.728	0.026	0.754	0.931	55.880	13.456%
60	0.710	0.644	0.033	0.677	0.836	50.186	22.274%
75	0.685	0.632	0.026	0.658	0.813	48.781	24.450%
90	0.623	0.574	0.024	0.599	0.739	44.352	31.309%
105	0.602	0.566	0.018	0.584	0.721	43.274	32.979%
120	0.554	0.521	0.017	0.538	0.664	39.845	38.290%
150	0.530	0.510	0.010	0.520	0.642	38.537	40.315%
180	0.488	0.450	0.019	0.469	0.579	34.764	46.158%
240	0.434	0.396	0.019	0.415	0.513	30.750	52.375%
300	0.404	0.382	0.011	0.393	0.486	29.133	54.880%
360	0.376	0.367	0.005	0.371	0.459	27.518	57.382%
420	0.354	0.331	0.011	0.343	0.423	25.405	60.654%
480	0.330	0.317	0.006	0.324	0.400	23.991	62.844%
540	0.316	0.293	0.012	0.305	0.376	22.572	65.041%
600	0.299	0.285	0.007	0.292	0.361	21.649	66.471%
1440	0.184	0.174	0.005	0.179	0.222	13.295	79.409%
2880	0.087	0.063	0.012	0.075	0.093	5.550	91.404%
4320	0.087	0.063	0.012	0.075	0.093	5.550	91.404%

Appendix Table A5 A 80 mg/L Cr(VI) removal by WTS/nZVI 1:1 composite from synthetic wastewater

Time (mins)	**Absorbance**				**Cr(VI) conc. (mg/L)**		**Removal percentage**
	1	**2**	**SD**	**Ave**	**Diluted conc.**	**conc.**	
0	0.816	0.829	0.006	0.823	1.016	81.274	0.000%
15	0.760	0.785	0.013	0.772	0.954	76.308	6.111%
30	0.747	0.749	0.001	0.748	0.924	73.909	9.062%
45	0.689	0.712	0.011	0.700	0.865	69.205	14.850%
60	0.671	0.704	0.016	0.687	0.849	67.913	16.440%
75	0.636	0.685	0.024	0.661	0.816	65.278	19.682%
90	0.632	0.668	0.018	0.650	0.803	64.221	20.982%
105	0.579	0.652	0.037	0.615	0.760	60.789	25.205%
120	0.568	0.635	0.034	0.602	0.743	59.437	26.868%
150	0.534	0.607	0.036	0.571	0.705	56.368	30.644%
180	0.515	0.596	0.041	0.555	0.686	54.870	32.488%
240	0.489	0.570	0.041	0.529	0.654	52.298	35.653%
300	0.481	0.539	0.029	0.510	0.630	50.364	38.032%
360	0.441	0.520	0.040	0.481	0.594	47.491	41.567%
420	0.462	0.534	0.036	0.498	0.615	49.182	39.486%
480	0.430	0.489	0.029	0.459	0.567	45.395	44.146%
540	0.440	0.495	0.027	0.468	0.577	46.200	43.156%
600	0.426	0.496	0.035	0.461	0.569	45.501	44.016%
1440	0.342	0.361	0.010	0.351	0.434	34.720	57.280%
2880	0.258	0.283	0.012	0.271	0.334	26.753	67.082%
4320	0.204	0.228	0.012	0.216	0.267	21.369	73.708%

Appendix Table A6 A pH3 Cr(VI) removal by WTS/nZVI 1:1 composite from synthetic wastewater

Time (mins)	Absorbance				Cr(VI) conc. (mg/L)		Removal percentage
	1	2	SD	Ave	Diluted conc.	conc.	
0	0.860	0.884	0.012	0.872	1.077	86.147	0.000%
120	0.366	0.289	0.038	0.328	0.405	32.372	62.422%
180	0.216	0.165	0.026	0.190	0.235	18.809	78.166%
240	0.145	0.093	0.026	0.119	0.147	11.785	86.320%
300	0.078	0.048	0.015	0.063	0.078	6.223	92.776%
360	0.043	0.030	0.006	0.037	0.045	3.626	95.791%
420	0.024	0.037	0.007	0.030	0.037	2.974	96.548%
480	0.017	0.023	0.003	0.020	0.025	2.006	97.672%

Appendix Table A7 A pH11 Cr(VI) removal by WTS/nZVI 1:1 composite from synthetic wastewater

Time (mins)	**Absorbance**				**Cr(VI) conc. (mg/L)**		**Removal percentage**
	1	**2**	**SD**	**Ave**	**Diluted conc.**	**conc.**	
0	0.818	0.858	0.020	0.838	1.034	82.752	0.000%
120	0.666	0.786	0.060	0.726	0.897	71.766	13.276%
180	0.655	0.750	0.048	0.703	0.868	69.423	16.107%
240	0.671	0.640	0.016	0.655	0.810	64.761	21.741%
300	0.651	0.537	0.057	0.594	0.734	58.686	29.082%
360	0.642	0.469	0.086	0.555	0.686	54.877	33.685%
420	0.227	0.218	0.004	0.223	0.275	22.008	73.405%
1620	0.209	0.219	0.005	0.214	0.265	21.162	74.427%
1680	0.202	0.209	0.004	0.205	0.254	20.301	75.467%
1800	0.818	0.858	0.020	0.838	1.034	82.752	0.000%

Appendix Table A8 A total chromium removal by WTS/nZVI 1:1 composite from authentic wastewater

Time	Total Cr Conc.					Removal	q
(min)	1	2	3	SD	Ave	Percentage	
0	358.700	368.400	353.900	6.031	360.333	0.000%	0.000
120	251.463	253.108	252.656	0.694	252.409	29.951%	107.924
240	166.844	168.461	167.252	0.687	167.519	53.510%	192.814
360	95.664	93.059	92.868	1.275	93.864	73.951%	266.470
480	54.996	56.053	55.372	0.437	55.474	84.605%	304.860
600	26.359	28.826	26.937	1.053	27.374	92.403%	332.959
720	10.275	11.176	10.745	0.368	10.732	97.022%	349.601
840	0.203	0.122	0.152	0.033	0.159	99.956%	360.174
960	0.175	0.143	0.078	0.040	0.132	99.963%	360.201
1080	0.124	0.151	0.106	0.018	0.127	99.965%	360.206

Appendix Table A9 A Pb(II) removal by WTS/nZVI 1:1 composite from synthetic wastewater

Time (min)	Pb(II) Conc.									
	100 mg/L		500 mg/L		1000 mg/L		1500 mg/L		2000 mg/L	
	Ave conc.	Removal percentage	Ave conc.	Removal percentage	Ave conc.	Removal percentage	Ave conc.	Removal percentage	Ave conc.	Removal percentage
0	98.030	0.000%	430.397	0.000%	878.427	0.000%	1451.510	0.000%	1903.050	0.000%
30	33.844	65.476%	334.425	22.298%	731.043	16.778%	1245.100	14.220%	1672.590	12.097%
60	0.124	99.874%	299.994	30.298%	709.946	19.180%	1194.910	17.678%	1661.610	12.674%
90	0.097	99.901%	252.091	41.428%	651.407	25.844%	1103.790	23.956%	1518.470	20.187%
120	0.055	99.944%	228.655	46.873%	635.902	27.609%	1045.190	27.993%	1457.580	23.384%
240	0.048	99.951%	129.752	69.853%	592.650	32.533%	885.324	39.007%	1343.380	29.378%
360	0.034	99.965%	59.093	86.270%	562.000	36.022%	851.068	41.367%	1301.700	31.566%
480	-	-	37.828	91.211%	551.800	37.183%	827.378	42.999%	1225.970	35.541%
1440	-	-	20.153	95.318%	-	-	815.875	43.791%	-	-
1560	-	-	1.795	99.583%	-	-	-	-	1157.670	39.127%
1680	-	-	1.509	99.649%	374.275	57.393%	-	-	-	-
1800	-	-	0.104	99.976%	-	-	-	-	1142.520	39.922%

Appendix B

The calculation of an amount of nZVI in the WTS/nZVI composite

An amount of $FeCl_3{\cdot}6H_2O$ and $NaBH_4$ for nZVI synthesis were calculated. An amount of nZVI was fix at 1.5 g for every ratio of WTS/nZVI composite. The ratio of an amount of $Fe(H_2O)_6^{3+}$: BH_4^- : Fe_0 was equal to 1:3:1.

For $FeCl_3$ solution preparation, the molecular weight of Fe is 55.85 g/mol. The concentration of $FeCl_3$ solution was 0.6 M (mol/L).

That means, in 0.6 m/L $FeCl_3$ solution 1 L, there is Fe 0.6 mol/L×55.85 g/mol = 33.51g/L

Fe 33.51 g can be prepared $FeCl_3$ solution for 1 L

If Fe 1.5 g can be prepared $FeCl_3$ solution for 1.5/33.51 = 0.04476 L or 44.76 mL

For $NaBH_4$ solution preparation, the molecular weight of BH_4^- is 14.52 g/mol. The concentration of $NaBH_4$ solution was 0.8 M (mol/L). According to the equation (7), that means 1.5g of Fe can be reacted with 4.5g of BH_4^-.

That means, in 0.8 m/L $NaBH_4$ solution 1 L, there is BH_4^- 0.8 mol/L×14.52 g/mol×3 = 35.62 g/L

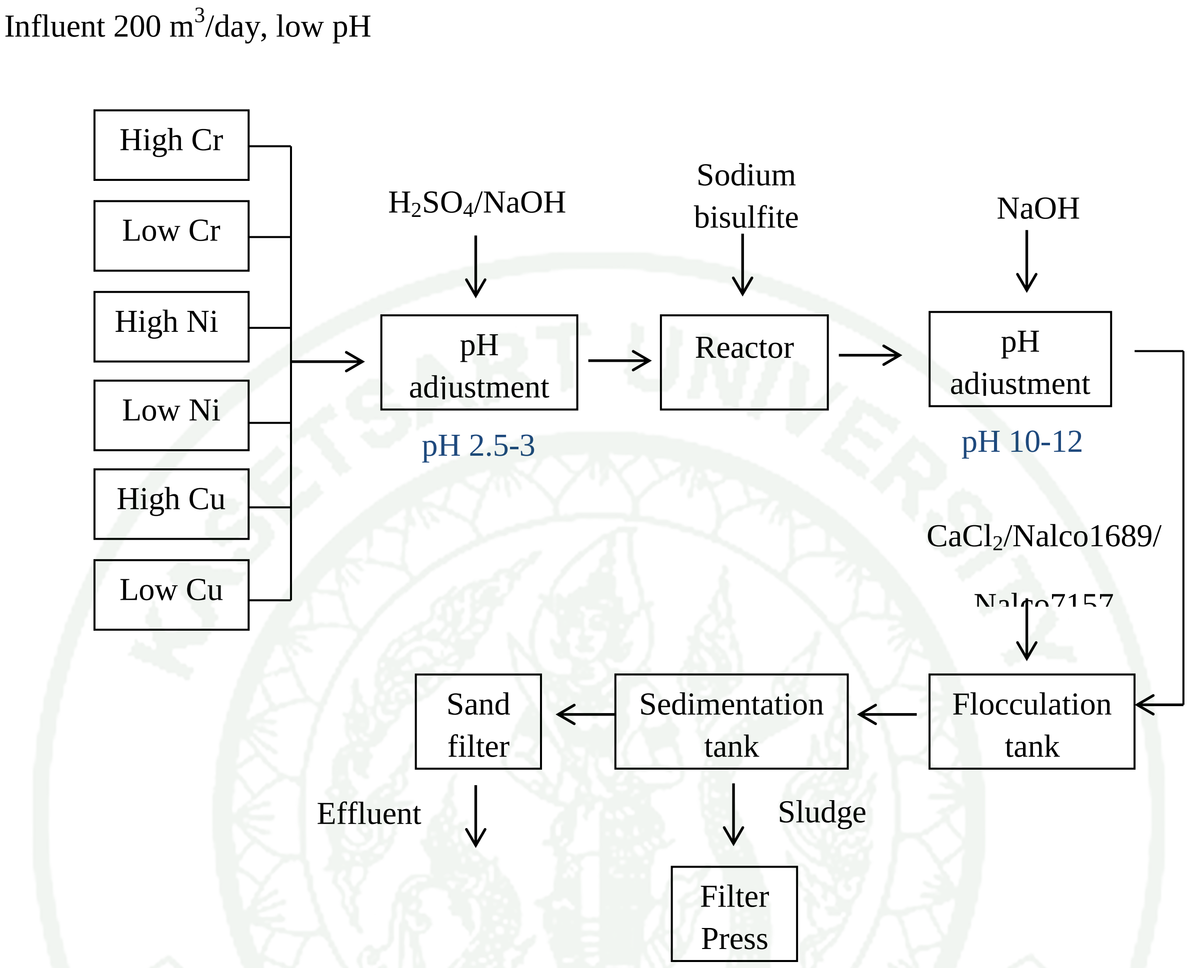
BH_4^- 35.62 g can be prepared $NaBH_4$ solution for 1 L

If BH_4^- 4.5 g can be prepared $NaBH_4$ solution for 4.5/35.62 = 0.12633 L or 126.33 mL

Appendix C

Figures of wastewater treatment plant, Sum Hitech Co., Ltd.

Appendix Figure C1 a) Rinsing chromium wastewater storage tank, b) Wastewater treatment units, c) Reduction tank, d) Sedimentation tank, e) Sand filter, f) Monitoring tank



Appendix Figure C2 The flow chart of electroplating wastewater treatment plant, Sum Hitech Co., Ltd.

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