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Development of Nano-Zero Valent Iron for the Remediation of Contaminated Water

Wan Zuhairi Wan Yaacob, Noraznida Kamaruzaman, Abdul Rahim Samsudin

Geology Program, School of Environmental Sciences and Natural Resources,
Faculty of Science and Technology, Universiti Kebangsaan Malaysia,
43600 Bangi, Selangor Darul Ehsan, Malaysia
drwzwy@gmail.com

Various materials are currently available to remove heavy metals from groundwater such as activated carbons, carbon nano tubes, bentonite and Zero Valent Iron (ZVI). All these materials are capable to transform toxic substances to non toxic and/or to adsorb toxic substances via ionic exchange, ion precipitation and adsorption. Nano-sized Zero Valent Iron (NZVI) is considered as an effective adsorbent and ideal technology for *in-situ* remediation of heavy metal contaminated groundwater. Therefore, this study was conducted to produce NZVI via chemical reduction process using $FeCl_2•4H_2O$ titrated with reduction agent of $NaBH_4$. The process is divided into four stages; mixing, separating, washing and drying. The materials produced from these processes are varies in colours, i.e. black, dark brown, brown and light brown. Colour variation observed is due to the intensity of oxidation process of these materials and became the main predicament of this research, especially during drying stage. Samples produced were marked according to their colours. The particle size of selected Zero Valent Iron samples namely ZVI-1b, ZVI-3b and ZVI-4b were determined using Master-sizer instrument. Sample ZVI-3b has a particle size ranging from 0.4 μm – 1000 μm and it is mainly dominated by 50 μm particles. ZVI-4b has the same size range as ZVI-3b but it is dominated mainly by particles of 60 μm. Meanwhile, the particle size for ZVI-1a could not be detected because of much smaller size which is well below the detection range of the size analyser. Another four samples namely ZVI-1a, ZVI-1b, ZVI-2b and ZVI-3b were analysed using Scanning Electron Microscopy (SEM). The results show that ZVI-1a has a platy texture, ZVI-1b has a dendritic texture and ZVI-2b has both platy and dendritic textures. While ZVI-3b shows a botryoidal texture. All results including colour, particle size and SEM images indicate that there is a potential of producing Nano-Zero Valent Iron especially ZVI-1b that has properties (size and micro texture) similar to Nano-Zero Valent Iron. Batch tests further confirmed the capability of ZVI-1b to effectively remove Cu from contaminated solution for up to 97 %.

1. Introduction

In recent years nano scale zero valent iron have received much attention for their potential application for the treatment of contaminated soils and water. According to Zhu et al. (2009), due to various technologies which are available to remove heavy metal from water, the nano scale zero valent iron is reported an ideal candidate for *in-situ* remediation because of its large active surface area and high heavy metal adsorption capacity. The Nano-Zero Valent Iron is capable to exchange the toxic

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substances to non toxic materials. Nano-Zero Valent Iron can also be used to promote the reduction and precipitation of toxic and carcinogenic metals such as chromium, Cr (VI) to more stable form of chromium, Cr (III) (Blowes et al., 2000). The preparation of Nano-Zero Valent Iron is normally conducted in two ways; by heating process using a mixture of iron oxide and carbon and lime powder (Uenosono et al., 2005) or by reduction of dissolved iron using a reducer to transform the dissolved metal into zero-valent iron (Panturu et al., 2010; Sun et al.,2007; Dickinson and Scott, 2010). This research aims to produce Nano-Zero Valent Iron using chemical reduction process, to characterise the properties of NZVI produced and to assess the capability of this material to treat contaminated groundwater.

2. Materials and Methods

Production of ZVI involved a reduction method using two main chemicals which were $FeCl_2.4H_2O$ and $NaBH_4$ followed the method proposed by Uzum et al. (2008). The $NaBH_4$ functions as a reducing agent in order to reduce the iron chloride ($FeCl_2.4H_2O$) in form of solution to produce zero valent iron. The method comprised of four stages which were mixing, separating, washing and drying. These two chemicals were mixed by dropping 1 M of sodium borohydride ($NaBH_4$) solution into 50 ml of 2 M $FeCl_2.4H_2O$ continuously while stirring the reaction mixture well. Excess $NaBH_4$ was typically applied in order to accelerate the reaction and ensured uniform growth of iron particles. The resulted reaction occurs as;

$$Fe^{2+} + 2BH^{4-} + 6H_2O \rightarrow FeO + 2B(OH)_3 + 7H_2\uparrow \text{ (Uzum et al., 2008)} \quad (1)$$

Immediately after the first drop of reducing agent into iron solution, black particle was appeared. Then further mixing for 15 to 20 min produce the maximum yield of black iron particles. Black iron particles were then separated from the solution by vacuum filtration using Whatmann cellulose nitrate membrane filter (0.45 um).

The most critical stages during preparation process of iron particles were washing and drying the iron particles. The washing stage was conducted using four different ways. They were; (i) washed five times with 30 mL of ethanol; (ii) rinsed three times with 30 mL of ethanol; (iii) washed with the mixture of 20 mL of ethanol and 20 mL of deionised water and (iv) washed three times with 30 ml deionised water and followed by 30 mL of ethanol. The drying process was carried out using three different ways; oven-dried for 24 h, using desiccator for 72 h and desiccator with vacuum pump for 24 h.

Table 1: Colour variations of Zero Valent Iron after different procedures of washing and drying.

Samples	Washing	Drying (duration)	Colour
NZVI-1a	5 times with 30 mL ethanol	Oven (24 h)	Dark brown
NZVI-1b	5 times with 30 mL ethanol	Desiccator (72 h)	Black
NZVI-2a	3 times with 30 mL ethanol	Oven (24 hours)	Dark brown
NZVI-2b	3 times with 30 mL ethanol	Desiccator (72 h)	Dark Brown
NZVI-2c	3 times with 30 mL ethanol	Desiccator connected to vacuum (24 h)	Light brown
NZVI-3a	20 mL ethanol and 20 mL of deionised water	Oven (24 h)	Light brown
NZVI-3b	20 mL ethanol and 20 mL of deionised water	Desiccator (72 h)	Brown
NZVI-4a	3 times 30 mL deionised water and followed by 30 mL ethanol	Oven (24 h)	Brown
NZVI-4b	3 times 30 mL deionised water and followed by 30 mL ethanol	Desiccator (72 h)	Brown

Cation Exchange Capacity (CEC) is the quantity of cations reversibly adsorbed per unit weight of mineral. The CEC was determined using batch tests with ammonium acetate exchange as described by ASTM D4319 (ASTM, 1984). The Specific Surface Area (SSA) was conducted using Laboratory

Manual of the Geotechnical Research Centre of McGill University, Montreal, Canada (unpublished). Batch equilibrium tests were carried out using a standard method reported by USEPA (1992) to determine the sorption capability of NZVI on copper (Cu). The test was carried out using 3g of NZVI in 30 mL of Cu at initial concentration of 450 mg/L. The pH was fixed at 4 and the sorption reaction was performed for 24 h.

3. Results and Discussions

Based on the washing and drying procedures that was previously explained above, the dried material of zero valent iron were divided into nine samples according to their colour variations such as black, brown, light brown and dark brown (Table 1). It was also observed that after separating zero valent iron particles from solution, all particles were turned to black. But, after drying, the colours of all zero valent iron materials were slowly changed to brown. This colour changes showed that most of the samples were easily oxidized during the drying stage. In order to prevent excessive oxidation, the drying stage was conducted under vacuum condition and this step was successfully prevented the oxidation of iron particles.

The particle size determination of the zero valent iron was performed using Master-sizer instrument. This instrument has a detection limit of 0.01 µm. The selected samples that were sent for particle analysis were NZVI-1b, NZVI-2b and NZVI-4b that represent the materials produced in the laboratory. The result showed that ZVI-2b gave a particle size ranged from 0.4 µm – 1000 µm with the highest percentage observed was at 50 µm (Figure 1). Data of ZVI-4b also gave the same range similar to ZVI-2b but had higher percentage of 60 µm particles (Figure 2). Meanwhile, particle size analysis for ZVI-1a has not produced any reading within the range of detection of the machine. This problem exists because the particle size for ZVI-1a is far below the detection limit of the instrument and indicates that ZVI-1b has particles finer than 0.01 µm and could be in the nano size range. This early conclusion about the size of ZV1-1b must be proven by using other sensitive instruments such as scanning electron microscope (SEM).

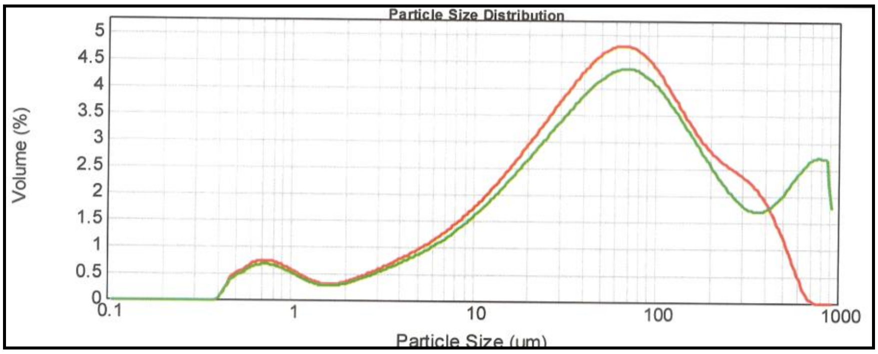

Figure 1: Result of particle size distribution of ZVI-2b sample using Master-sizer

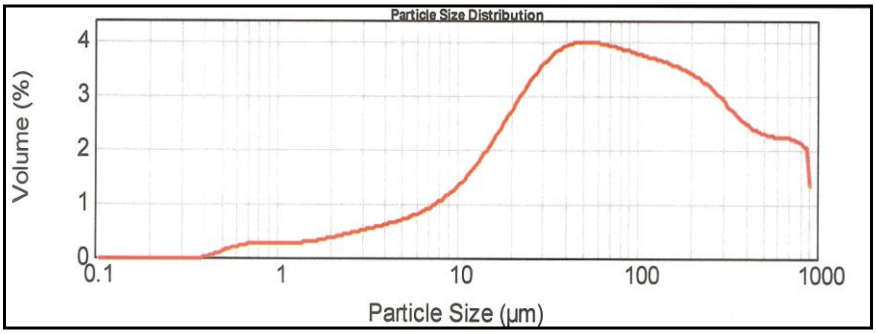

Figure 2: Result of particle size distribution of ZVI-4b sample using Master-sizer

Four samples namely ZVI-1a, ZVI-1b, ZVI-2b and ZVI-3b were then photographed using Scanning Electron Microscopy (SEM). This instrument is used to determine the texture of crystal growth and could also indirectly use to measure the particle size of the materials. SEM images show that the surface crystal growth textures of NZVI are varied and these variations could possibly be due to the variations in the preparation methods used in this study. NZVI-1a has a platy texture (Figure 3). NZVI-1b showed a dendritic texture (Figure 4). NZVI-2b has both platy and dendritic textures (Figure 5). Meanwhile, NZVI-3b showed a botryoidal texture (Figure 6). Most of the NZVI particles are in nano scale (can be seen on the scale bar at the bottom left of the SEM image). Sample NZVI-1a in Figure 3 shows very clearly that the platy texture of this NZVI has the nano particle size which is within 100 nm. According to Panturu et al. (2010), the particle size distribution obtained in their study was 211.5 nm and was greatly influenced by the intensity and volume. Another study conducted by Ponder et al. (2000) gave an estimation of the average iron particle diameter of 10-30 nm. Sun et al. (2007) stated that the particle size of iron nano particles ranged from tens to hundreds of nanometers. Therefore, the particle size of iron nanoparticles produced in this study, measured by SEM images are less than 100 nm.

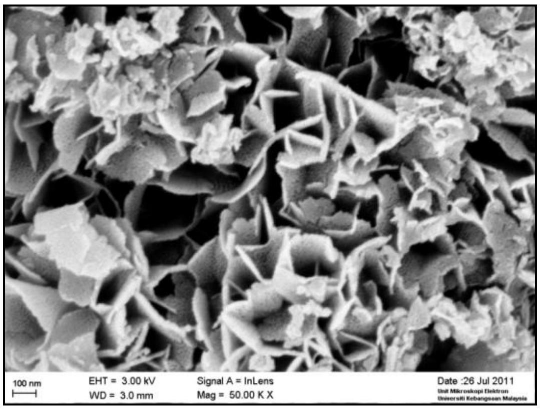

Figure 3: SEM microimage showing platy crystal growth of ZVI-1a

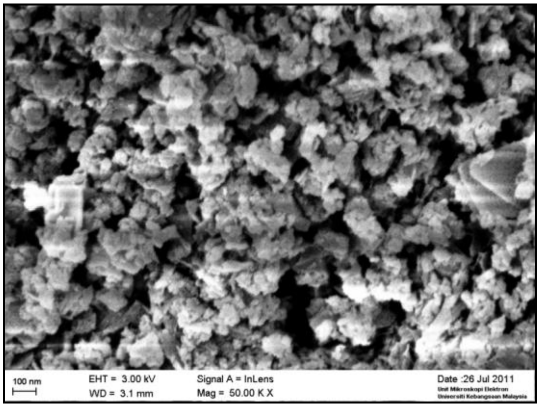

Figure 4: SEM image showing dendritic texture of ZVI-1b

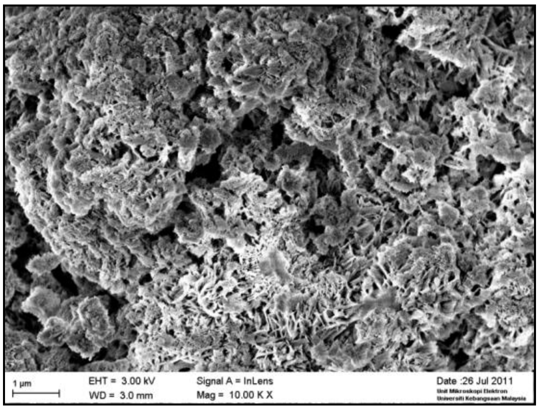

Figure 5: SEM image of ZVI-2b showing the dendritic crystal texture

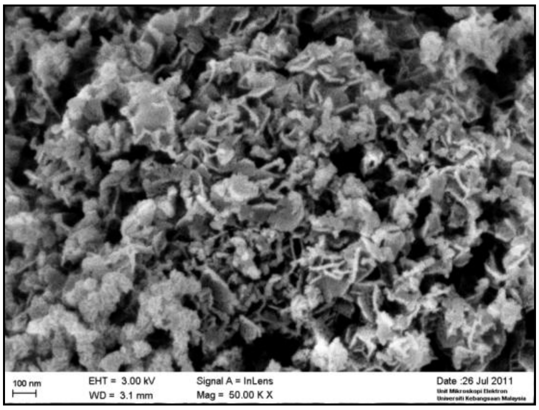

Figure 6: SEM image showing the botryoidal texture of ZVI-3b

Table 2 below shows the property of Cation Exchange capacity (CEC) and Specific surface Area (SSA) of Nano-Zero Valent Iron produced in this study. Four samples were selected to measure the CEC and SSA, namely NZV1-1b, NZV1-2b, NZV1-3b and NZV1-4b. The results showed that sample NZVI-2b has the highest CEC value compared to other samples, with the value of 9.93 meq/100g. NZVI-1b has the lowest CEC value. Surprisingly, the SSA is not correlated with the CEC values. The SSA value is observed to be very high for sample NZVI-1b with the value of 278.8 m^2/g. This SSA value is supported by the particle size for NZVI-1b which is very fine and below the detection limit of the Master-sizer instrument. The lowest SSA value was given by sample NZVI-2b, with the value of 161.2 m^2/g.

Table 2: The CEC and SSA values for NZVI materials produced in this study

Sample	CEC (meq/100 g)	SSA (m^2/g)
NZVI-1b	1.129	279.8
NZVI-2b	9.930	161.2
NZVI-3b	3.850	192.4
NZVI-4b	2.060	233.0

Batch experiment was conducted by mixing copper (Cu) solution at initial concentration of 450 mg/l. The pH of the solution was fixed at 4 and agitated for 24 hours. The results of sorption are presented in Table 3. The results show very clearly that sample NZVI-1b which has finer particles and higher SSA absorbed more Cu compared to other materials. The percentage of sorption for Cu by NZVI-1 was calculated to be 97 %. This is followed by sample NZVI-4b (75 %), NZVI-3b (53 %) dan NZVI-2b (38 %).

Table 3. The sorption percentage of Cu by all NZVI materials

Samples	C_O (mg/L)	C_F (mg/L)	q_e (mg/kg)	Sorption (%)
NZVI-1b	450	13.85	4.36	97
NZVI-2b	450	281.0	1.69	38
NZVI-3b	450	174.1	2.76	53
NZVI-4b	450	113.5	3..37	75

4. Conclusion

The study concludes that Nano-Zero Valent Iron has been successfully synthesised in the laboratory using iron chloride and sodium borohydride. The study also discovered a new technique to prevent immediate oxidation of zero valent iron produced, i.e. by washing 5 times with 30 mL ethanol and drying for 72 h in the desiccator. NZVI-1b is considered as Nano-Zero Valent Iron material as shown by its nano scale particles (i.e. less than100 nm) with dendritic texture of crystal growth and posses high SSA but relatively small CEC values. This material is also capable to remove large amount of Cu from Cu contaminated water for up to 97 %.

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