

Synthesis of Bimetallic Fe/Cu Nanoparticles with Different Copper Loading Ratios

May Thant Zin, Josephine Borja, Hirofumi Hinode, Winarto Kurniawan

Abstract—Nanotechnology has multiple and enormous advantages for all application. Therefore, this research is carried out to synthesize and characterize bimetallic iron with copper nanoparticles. After synthesizing nano zero valent iron by reduction of ferric chloride by sodium borohydride under nitrogen purging environment, bimetallic iron with copper nanoparticles are synthesized by varying different loads of copper chloride. Due to different standard potential (E^0) values of copper and iron, copper is coupled with iron at (Cu to Fe ratio of 1:5, 1:6.7, 1:10, 1:20). It is found that the resulted bimetallic Fe/Cu nanoparticles are composing phases of iron and copper. According to the diffraction patterns indicating the state of chemical combination of the bimetallic nanoparticles, the particles are well-combined and crystalline sizes are less than 1000\AA (or 100nm). Specifically, particle sizes of synthesized bimetallic Fe/Cu nanoparticles are ranging from 44.583 nm to 85.149 nm.

Keywords—Bimetallic Fe/Cu nanoparticles, Loading ratio, Synthesis.

I. INTRODUCTION

ZERO valent iron (ZVI) has become attractive in the degradation of chlorinated contaminants such as DDT because of its potential to remove all the chlorines much faster than natural process under moderate conditions [1], [2]. In the degradation of pollutants such as DDT [3], several types of iron particles such as low cost iron [3], micro-scale ZVI [4], [5], nano-scale ZVI [6]-[8], bimetal Pd/Fe [9], Ni/Fe [8], and Co/Fe [10], [11] have been used.

Studies have shown that the effects of the second metal vary with the choice of the second metal. In addition, the amount of the second metal in relation to the iron particles is also crucial in the overall rate of contaminant degradation.

Normally, metallic nanoparticles can be synthesized by top-down methods and bottom-up methods. The former methods apply the mechanical grinding of bulk metals and subsequent stabilization of the resulting nanosize metal particles and the weak point is that it is hard to obtain narrow particle size distributions. Likewise, nanoparticles can be produced, according to bottom-up methods, by starting from either atomic or molecular precursors in gas or solution [10]. However it is unable to yield simultaneous control over

May Thant Zin is with De La Salle University, Manila, Philippines and Tokyo Institute of Technology, Tokyo, Japan (mobile: +818044047384, +61-9159395890; phone and fax: +81-3-57343245; e-mail: mtz.cmu@gmail.com).

Josephine Borja is with Department of Chemical Engineering, De La Salle University, Manila, Philippines.

Hirofumi Hinode is with Department of International Development Engineering, Tokyo Institute of Technology, Tokyo, Japan.

Winarto Kurniawan is an assistant professor at Department of International Development Engineering, Tokyo Institute of Technology, Tokyo, Japan.

nanoparticle structure, surface chemistry, monodispersity, crystal structure and assembly. In reality, the characteristics and properties of NZVI produced can be affected by the synthesis process. There are four main steps in the synthesis of nZVI: supersaturation of the solution, nucleation of the NZVI cluster, growth of NZVI nuclei, and agglomeration of NZVI [6], [12].

When potassium borohydride was used and the whole process for syntheses was carried out under a flow of Ar gas, particle size of ZVI produced was 80nm. The particle size of ZVI synthesized from sodium borohydride and ferric solution in nitrogen environment is 60nm [12]. Therefore, it is relevant to use sodium borohydride in this research in order to get smaller particle size in comparison with potassium borohydride. Generally, ZVI particles produced by the borohydride reduction method (BRM) usually have the sizes of nano or micro scales and surface areas of 20-40 m^2/g and also give 10 to 1000 times greater reactivity compared with granular ZVI.

Table I shows some of the laboratory-synthesized zero valent iron (ZVI), nano zero valent iron (NZVI) and ZVI-based materials [13]-[19]. In addition, Table II summarizes some of the commercially available ZVI.

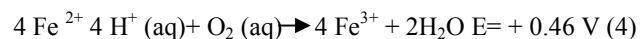
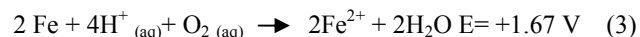
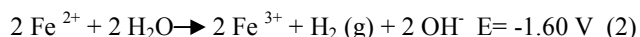
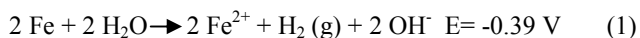
TABLE I
LABORATORY-SYNTHESIZED ZVI, NZVI AND ZVI-BASED MATERIALS [13]-[19]

Method	Dimensions	Surface area	Reference
Borohydride reduction method (BRM)	10-50 nm	24.4 m^2/g	[14]
BRM	<100 nm	35 m^2/g	[6]
BRM	12 nm	45.4 m^2/g	[15]
BRM	20-90 nm	39.94-54.04 m^2/g	[16]
Carbothermal reduction method (CRM)	20-150 nm	38-130 m^2/g	[17]
Mixing-pelletization	0.85-6.7 mm	not available	[18]
Mechanical alloying	20- 100 μm	16 m^2/g	[19]

TABLE II
COMMERCIALY AVAILABLE ZVI [13]

Supplier	Dimensions	Surface area
Sicalab	20-100 μm	0.1 m^2/g
RDH Chemical	212 μm	0.183 m^2/g
BASF	0.77 μm	not available
Merck	<0.150 μm	0.1 m^2/g
Shinyo Pure Chemical	196.46 μm	0.065 m^2/g
Nanjing	65.3 nm	not available
Aesar	<75 μm	0.359 m^2/g
Peerless Metal Powders and Abrasive	195.37 μm	0.055 m^2/g
J.T. Baker	245 μm	20.78 m^2/g

Iron (Fe) is easy to undergo corrosion in aqueous solution and as a result, electrochemical processes can be occurred. They are likely to occur as the following equations depending on the condition such as acidity of the solution:



Again hydroxide ion and ferric ion can combine and form iron (III) oxide-hydroxide form.

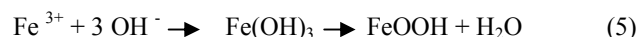


TABLE III
USE OF SOME BIMETALLIC NANOPARTICLES IN DEGRADATION OF POLLUTANTS

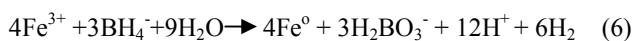
Study	Significant results	Reference
Use of Fe/Pd	67%-82% for the TCE in soil	[20]
Use of Fe/Pd immobilized on an alginate bead	removal rate of 96% TCE was achieved after 1h degradation process; 4h 99.8% removal rate	[21]
NZVI with the presence of vitamin B ₁₂	96% of the PCE transformed to its byproducts during a 6h period	[22]
Use of Fe/Pd to treat TCE, PCE and TCA	Removal efficiency: 85% TCE, 80% PCE and 56% TCA	[23]

There are various attempts, uses and applications of bimetallic nanoparticles. On the treatment of chlorinated organic contaminant TCE, it found that TCE is completely dechlorinated by Pd/Fe within 0.25 h [11]. Other uses of bimetallic nanoparticles on degradation of pollutants are summarized in Table III.

II. MATERIALS AND METHODS

A. Nano Zero Valent Iron (NZVI) Particles

The reaction for synthesis of nano zero valent iron (NZVI) can be described as the following equation [24], [25].



The following method, that is adapted from [10], [24], and [25], is applied to synthesize NZVI due to its simplicity, cost effectiveness and ability to handle easily.

To synthesize Nanoscale Zero Valent Iron (NZVI), 1L of 0.018 M ferric chloride solution is prepared by dissolving 4.869 g FeCl₃.6H₂O in 1L of 9/1 (v/v) ethanol/water mixture (900ml ethanol + 100ml deionized water) in a three-necked flask of 1L volume and stirring well with mechanic stirrer. At the same time, 2.8g NaBH₄ is dissolved in 100ml of deionized water to get sodium borohydride solution and the solution will then become hot due to exothermic reaction. Excess reagent borohydride will be used because better growth of iron nanoparticles needs excess borohydride. Nitrogen gas is being purged during synthesis process to evacuate oxygen and prevent the oxidation of NZVI during synthesis. Then, the

borohydride solution is added drop by drop at a rate of 7 to 7.5 ml per minute into iron chloride solution with vigorous stirring or mixing machine.

Just after the first drop of sodium borohydride solution, black solid particles are immediately appeared and then the remaining sodium borohydride is added completely to accelerate the reduction reaction. In addition, the mixture is left for another 10 minutes of stirring after adding the whole borohydride solution.

After that, the solid particles need to remove all of the water and therefore they are washed three times with absolute ethanol. This washing process is probably the vital step of synthesis due to the prevention of the rapid oxidation of zero valent iron nanoparticles.

Finally, the synthesized nanoparticles are undergone to freeze-drier. For storage, the NZVI is kept in vials that are put inside sealed bags in desiccators.

Actually, the complete reduction of 0.05 mol of Fe³⁺ requires only 0.0375 mol of BH₄⁻. The excessive borohydride is to accelerate the synthesis reaction.

Fig. 1 shows the flowchart of the synthesis of nano zero valent iron (NZVI) as well as synthesis of bimetallic Fe/Cu nanoparticles.

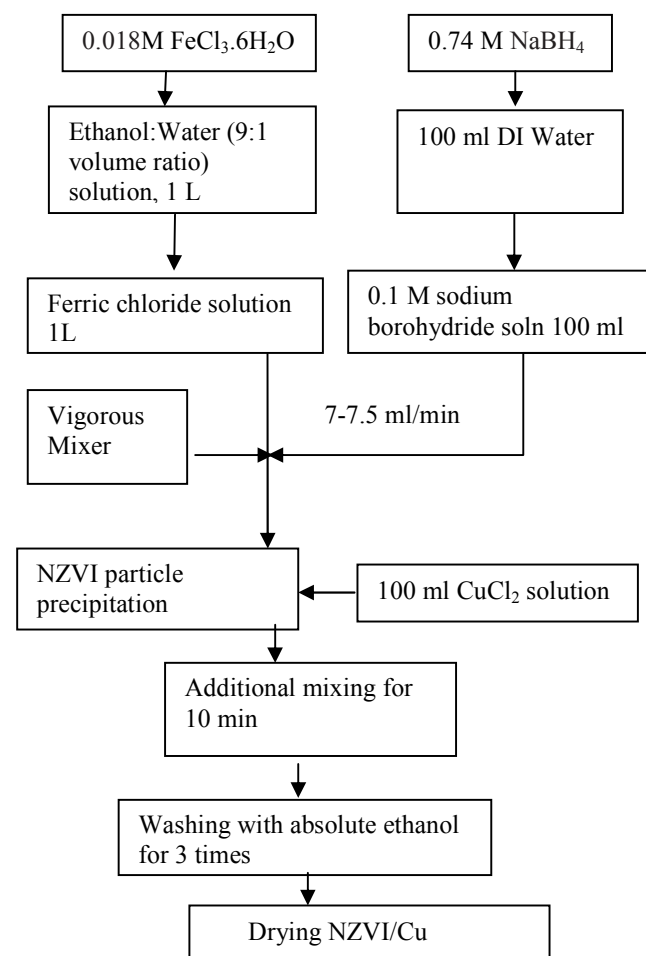


Fig. 1 Flowchart of Synthesis of Bimetallic Fe/Cu Nanoparticles

B. Bimetallic Nanoparticles

The bimetallic Fe/Cu nanoparticles are prepared by modifying the procedures in [26] and [27]. The particles have an NZVI core with a discontinuous Cu shell. Bimetallic nano-Fe/Cu particles are synthesized by addition of freshly prepared Fe⁰ particles into CuCl₂ solution in vigorous stirrer and ambient temperature. CuCl₂ solution is prepared by mixing CuCl₂·2H₂O with ethanol-water (9:1) solution. The percentage of Cu content can be changed during synthesis. The amount of copper coupling to NZVI is depending on the desired weight ratio of copper to iron. In this research, Cu to Fe ratio of 1:5, 1:6.7, 1:10, 1:20 (w/w) are chosen as the trace amount of second metal may enhance to increase the reactivity of the nanoparticles. The ratio is totally based on weight ratio of copper to iron. The particles are then washed with ethanol for three times and dried at freeze-drier.

C. Structure and Characterization of Bimetallic Fe/Cu Nanoparticles and NZVI

The investigation of nanostructures is a highly topical field in nano engineering. Some sophisticated characterization methods have been successfully developed during the last twenty years. In terms of characterization methods, NZVI can be characterized by many methods by X-ray Diffraction (XRD), transmission electron microscopy (TEM), particle size distribution (PSD) analysis and the Brunauer-Emmett-Teller (BET) surface area method so that the particle size, size distribution and morphology can be detected. One of those is the transmission electron microscope (TEM). TEM is an imaging technique. TEM image is formed by transmitting a beam of electrons through a specimen and then the image is magnified and directed either to be detected by a sensor to describe the NZVI surfaces or to appear on a fluorescent screen or layer of photographic film. TEM analysis will also show the morphology of synthesized nano particles (Rieth, 2003 and Lin et al., 2008). The size of the synthesized nZVI and bimetallic nZVI/Cu will be measured by using particle size distribution (PSD) analyzer and also high resolution transmission electron microscopy (TEM). TEM images will show if the synthesized NZVI appear as single particles or tend to agglomerate to create the nanoclusters because NZVI has the magnetic and electrostatic properties inherent in it and the NZVI usually tends to agglomerate [20], [25].

Even scattering methods (for example, X-rays) which is hard to beat have been improved. Moreover, microscopic information with high resolution has become available through the use of synchrotron radiation sources [13]. XRD scanning range can be acceptable if it covers all major species of iron and its compounds. XRD reveals information about the chemical composition and crystallographic structure of the synthesized NZVI and bimetallic NZVI/Cu particles [20], [25] and [28].

Specific surface area of the nanoparticles can be determined with the BET method. The systematic sorption and desorption of nitrogen in NOVA 1000e analyzer will result BET isotherm and consequently provide the fundamental information on the surface characteristics- the total surface area [26].

III. RESULTS AND DISCUSSIONS

When different copper ratios to nano zero valent iron, i.e., Cu to Fe ratio of 1:20, 1:10, 1: 6.7 and 1: 5 (w/w), have been applied to synthesize bimetallic nanoparticles of iron with copper, the different median diameters are found as 44.583nm, 59.220nm, 72.085nm, and 85.149nm, respectively, according to particle size distribution (PSD) analyses by PSD analyzer HORIBALA- 920 at circulation speed 5 with Laser T 88.9 % and ultrasonic 01:00(3).

The TEM images of synthesized bimetallic Fe/Cu nanoparticles are shown in the following figures from 2 to 5.

TEM images of synthesized nanoparticles show single particles as well as tendency to agglomerate to create the nanoclusters.

It can be due to different surface energies of copper and iron, the element with lower surface energy has tendency to segregate onto the surface. According to [29], by cluster expansion, surface energy of Cu is 1.377 eV atom⁻¹ and that of Fe is 2.613 eV atom⁻¹.

Normally, there is another explanation for the structure formation and that is the difference between atomic radii of two metals. However, atomic radii of iron and copper are not different much.

Therefore, the formation of bimetallic structure may also result from electron transfer from less to more electronegative elements.

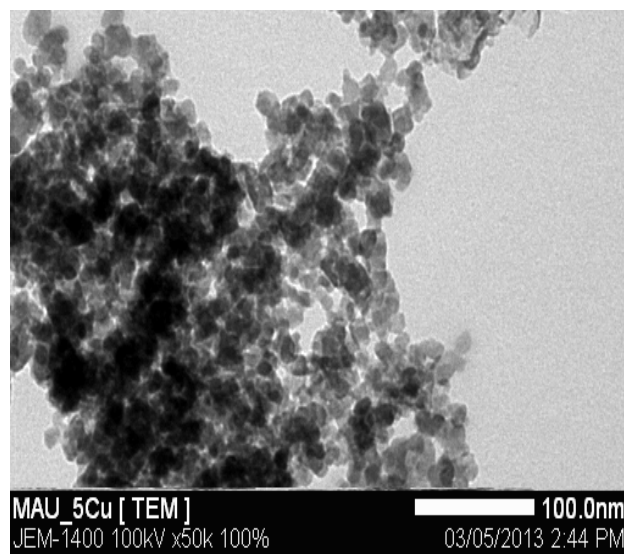


Fig. 2 TEM image of bimetallic Fe/Cu nanoparticles with Cu to Fe ratio of 1:20

According to TEM images, with the least amount of second metal, copper, on iron particles, the bimetallic Fe/Cu nanoparticles give the least agglomeration among the synthesized particles. Fig. 2 gives the clear crystalline structure of synthesized bimetallic Fe/Cu nanoparticles.

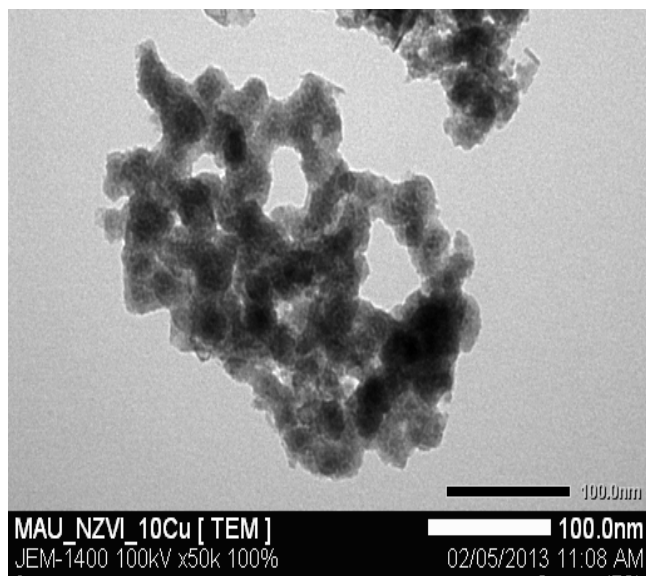


Fig. 3 TEM image of bimetallic Fe/Cu nanoparticles with Cu to Fe ratio of 1:10

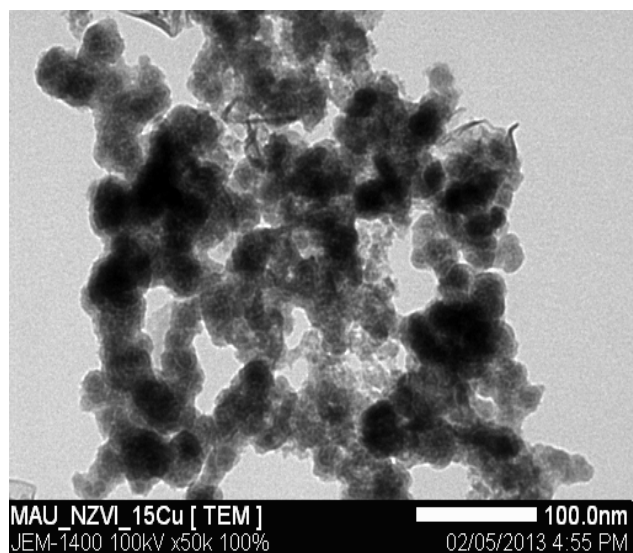


Fig. 4 TEM image of bimetallic Fe/Cu nanoparticles with Cu to Fe ratio of 1:6.7

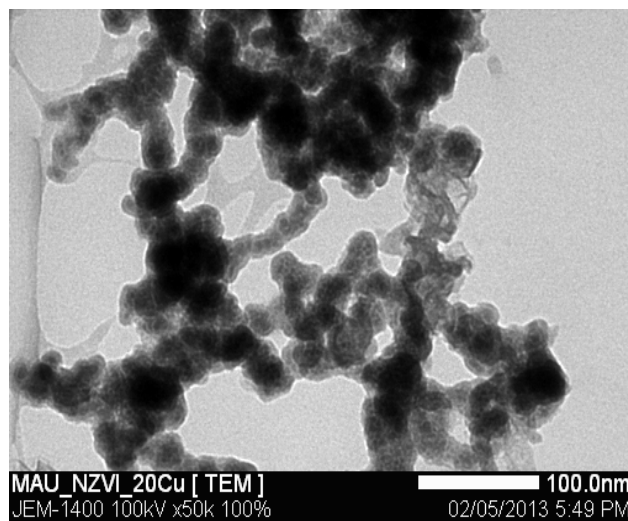


Fig. 5 TEM image of bimetallic Fe/Cu nanoparticles with Cu to Fe ratio of 1:5

The structures of synthesized bimetallic particles are complicated but they can be found in combination with core-shell segregated structures and intermetallic or alloyed structures (Figs. 2 to 5).

Fig. 6 shows the XRD peaks of synthesized bimetallic Fe/Cu nanoparticles. According to XRD analyses of synthesized bimetallic Fe/Cu nanoparticles, the peaks are composing phases of iron and copper.

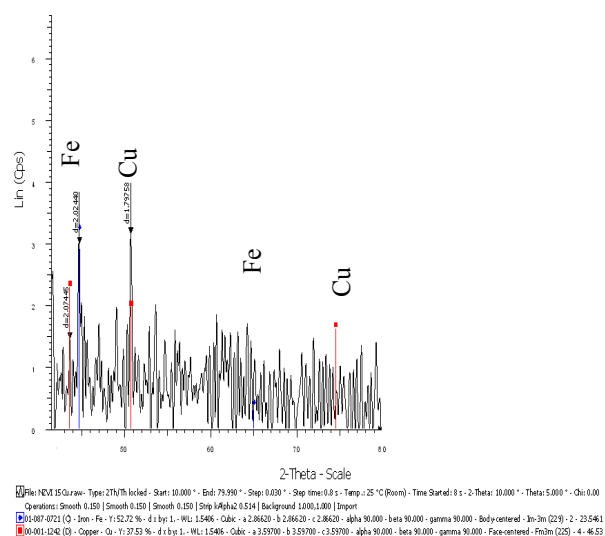


Fig. 6 XRD peaks of bimetallic Fe/Cu nanoparticles Cu to Fe ratio of 1:6.7

Moreover, surface areas of NZVI and bimetallic Fe/Cu particles are detected by using Quantachrome instruments. Multi-point BET plot shows that the surface areas of the bimetallic particles are ranging from 44.02 m²/g to 55.247 m²/g.

IV. CONCLUSIONS

This experimental study aims to synthesize and characterize nano zero valent iron particles as well as bimetallic iron with copper nanoparticles. The results reveal that the synthesized nano particles are within nano ranges. Synthesized bimetallic Fe/Cu nanoparticles with different Cu to Fe ratio of 1:20, 1:10, 1: 6.7 and 1: 5 (w/w) are found as 44.583 nm, 59.220 nm, 72.085 nm, and 85.149 nm. However, these particles are still necessary to reduce their tendency to agglomeration. Therefore, it is recommended that synthesized bimetallic particles shall be continued to undergo to encapsulation process.

ACKNOWLEDGMENT

This research is done with the scholarship from AUN/SEED-Net/ JICA.

REFERENCES

- [1] J. M. Aislabie, N.K. Richards, and H.L. Boul, "Microbial degradation of DDT and its residues-a review", *New Zealand Journal of Agricultural Research*, vol. 40, 1997, pp. 269-282.
- [2] D. G. Sayles, G. You, M. Wang, and M. J. Kupferle, "DDT, DDD, and DDE dechlorination by zerovalent iron", *Environmental Science and Technology*, vol. 31, 1997, pp. 3448-3454.
- [3] T. Satapanajaru, P. Anurakpongatorn, Songsasen, A., H. Boparai, and J. Park, "Using low-cost iron byproducts from automotive manufacturing to remediate DDT", *Water, Air, and Soil Pollution*, 175(1-4), 2006, pp 361-374.
- [4] D. G. Sayles, G. You, M. Wang, and M. J. Kupferle, "DDT, DDD, and DDE dechlorination by zerovalent iron", *Environmental Science and Technology*, 31, 1997, pp. 3448-3454.
- [5] T. Eggen, and A. Majcherczyk, "Effects of zero-valent iron (Fe⁰) and temperature on the transformation of DDT and its metabolites in lake sediment", *Chemosphere*, 62, 2006, pp. 1116-1125
- [6] Y. Sun, X. Li, J. Cao, W. Zhang, and H. P. Wang, "Characterization of zero-valent iron nanoparticles" *Advances in Colloid and Interface Science*, vol.120, 2006, pp. 47-56.
- [7] Q. N. M. Tran, "Degradation of DDT by Sequential NZVI-biofilm Process", M.S. thesis, De La Salle University, 2012.
- [8] H. Tian, J. Li, Z. Mu, L. Li, and Z. Hao, "Effect of pH on DDT degradation in aqueous solution using bimetallic Ni/Fe nanoparticles" *Separation and Purification Technology*, 66, 2009, pp. 84-89.
- [9] W. X. Zhang, C. B. Wang, and H.L. Lien, "Treatment of chlorinated organic contaminants with nanoscale bimetallic particles", *Catal. Today*, 40, 1998, pp. 387-395.
- [10] Y. Ju-Nam, and J. R. Lead, "Manufactured nanoparticles: An overview of their chemistry, interactions and potential environmental implications", *Science of the Total Environment*, vol. 400, 2008, pp. 396-414.
- [11] L. M. Cangco, B. M. C. Chan, and K. T. A. Chua, "Effect of cobalt in DDT degradation using emulsified and non-emulsified zero-valent iron (ZVI)", B. S. Thesis, De La Salle University, Manila, 2012.
- [12] W. X. Zhang, C. B. Wang, and H. L. Lien, "Treatment of chlorinated organic contaminants with nanoscale bimetallic particles", *Catal. Today*, vol. 40, 1998, pp. 387-395.
- [13] M. Gheju, "Hexavalent chromium reduction with zero-valent iron (ZVI) in aquatic systems", *Water Air Soil Pollut*, 2011, 222, 103-148.
- [14] B. A. Manning, J.R. Kiser, H. Kwon, and S.R. Kanel, "Spectroscopic investigation of Cr(III)- and Cr(VI)-treated nanoscale zerovalent iron", *Technology*, 2007, 41, pp. 586-592.
- [15] R. Singh, V. Misra, and R.P. Singh, "Synthesis, characterization and role of zero valent iron nanoparticle in removal of hexavalent chromium from chromium-spiked soil", *Journal of Nanoparticle Research*, 13(9), 2011, pp. 4063-4073.
- [16] L. Shi, X. Zhang, and Z. Chen, "Removal of chromium (VI) from wastewater using bentonite supported nanoscale zero-valent iron", *Water Research*, 45(2), 2011, pp. 886-892.
- [17] L. B., Hoch, E. J. Mack, B. W. Hydytsky, J. M. Hershman, J.M. Skluzacek and T.E. Mallouk, "Carbothermal synthesis of carbon-supported nanoscale zero-valent iron particles for the remediation of hexavalent chromium", *Environmental Science and Technology*, 42 (7), 2008, pp. 2600-2605.
- [18] Z. Li, H. K. Jones, P. Zhang, and R. S. Bowman, "Chromate transport through columns packed with surfactant-modified zeolite/ zero valent iron pellets", *Chemosphere*, 68(10), 2007, pp. 1861-1866.
- [19] F. d. S. Coelho, J.D. Ardisson, F.C.C. Moura, Lago, R. M., Murad, E., and Fabris, J. D. Potential application of highly reactive Fe (0)/ Fe₃O₄ composites for the reduction of Cr (VI) environmental contaminants, *Chemosphere*, 71(1), 2008, pp. 90-98.
- [20] W. Zhang, "Nanoscale iron particles for environmental remediation: An overview", *Journal of Nanoparticles Research*, vol. 5, 2010, pp. 323-332.
- [21] H. Kim, H. Hong, J. Jung, S. Kim, and J. Yang, "Degradation of trichloroethylene (TCE) by nanoscale zero-valent iron (nZVI) immobilized in alginate bed", *Journal of Hazardous Materials*, 176 (1-3), 2010, pp. 1038-1043.
- [22] A. Amir, and W. Lee, "Enhanced reductive dechlorination of tetrachloroethene by nano-sized zero valent iron with vitamin B₁₂", *Chemical Engineering Journal*, 170(2-3), 2011, pp. 492-497.
- [23] Y. Cho, and S. Choi, "Degradation of PCE, TCE and 1,1,1-TCA by nanosized FePd bimetallic particles under various experimental conditions", *Chemosphere*, 81(7), 2010, pp. 940-945.
- [24] Y. Hwang, D. Kim, and H. Shin, "Effects of synthesis conditions on the characteristics and reactivity of nano scale zero valent iron", *Applied Catalysis B: Environmental*, 105(1-2), 2011, pp. 144-150.
- [25] Z. Wang, P. Peng, and W. Huang, "Dechlorination of hexachlorocyclohexane by zero-valent metallic iron", *Journal of Hazardous Material*, vol.166, 2009, pp. 992-997.
- [26] K. S. Lin, N. B. Chang, and T.D. Chuang, "Fine structure characterization of zero-valent iron nanoparticles for decontamination of nitrites and nitrates in wastewater and groundwater", *Science and Technology of Advanced Materials*, vol. 9, 2008, pp. 025015.
- [27] S. M. Hosseini, B. Ataie-Ashtiani, and M. Kholghi, "Nitrate reduction by nano-Fe/Cu particles in packed column", *Desalination*, 276, 2011, pp. 214-221
- [28] R. Yuvakkumar, V. Elango, V. Rajendran, and N. Kanan, "Preparation and characterization of zero valent iron nanoparticles", *Digest Journal of Nanomaterials and Biostructures*, 6(4), 2011, pp. 1771-1776.
- [29] L. Vitos, A.V. Ruban, H. L. Skriver, and J. Kollar, "The surface energy of metals", *Surface Science*, 411(1-2), 1998, pp. 186-202.