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°) 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 1000Å (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 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 m²/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>
<thead>
<tr>
<th>Method</th>
<th>Dimensions</th>
<th>Surface area</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BRM</td>
<td>&lt;100 nm</td>
<td>35 m²/g</td>
<td>[6]</td>
</tr>
<tr>
<td>BRM</td>
<td>12 nm</td>
<td>45.4 m²/g</td>
<td>[15]</td>
</tr>
<tr>
<td>BRM</td>
<td>20-90 nm</td>
<td>39.94-54.04 m²/g</td>
<td>[16]</td>
</tr>
<tr>
<td>Carbothermal reduction method (CRM)</td>
<td>20-150 nm</td>
<td>38-130 m²/g</td>
<td>[17]</td>
</tr>
<tr>
<td>Mixing-pelletization</td>
<td>0.85-6.7 mm</td>
<td>not available</td>
<td>[18]</td>
</tr>
<tr>
<td>Mechanical alloying</td>
<td>20-100 µm</td>
<td>16 m²/g</td>
<td>[19]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Dimensions</th>
<th>Surface area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sicalab</td>
<td>20-100 µm</td>
<td>0.1 m²/g</td>
</tr>
<tr>
<td>RDH Chemical</td>
<td>212 µm</td>
<td>0.183 m²/g</td>
</tr>
<tr>
<td>BASF</td>
<td>0.77 µm</td>
<td>not available</td>
</tr>
<tr>
<td>Merck</td>
<td>&lt;0.150 µm</td>
<td>0.1 m²/g</td>
</tr>
<tr>
<td>Shinoya Pure Chemical</td>
<td>196.46 µm</td>
<td>0.065 m²/g</td>
</tr>
<tr>
<td>Nanjing</td>
<td>65.3 nm</td>
<td>not available</td>
</tr>
<tr>
<td>Aesar</td>
<td>&lt;75 µm</td>
<td>0.359 m²/g</td>
</tr>
<tr>
<td>Peerless Metal Powders and Abrasive</td>
<td>195.37 µm</td>
<td>0.055 m²/g</td>
</tr>
<tr>
<td>J.T. Baker</td>
<td>245 µm</td>
<td>20.78 m²/g</td>
</tr>
</tbody>
</table>

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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:

\[
2 \text{Fe} + 2 \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{2+} + \text{H}_2(g) + 2 \text{OH}^- \quad E = -0.39 \text{ V} \quad (1)
\]

\[
2 \text{Fe}^{2+} + 2 \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{3+} + \text{H}_2(g) + 2 \text{OH}^- \quad E = -1.60 \text{ V} \quad (2)
\]

\[
2 \text{Fe} + 4 \text{H}^+ (aq) + \text{O}_2 (aq) \rightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O} \quad E = +1.67 \text{ V} \quad (3)
\]

\[
4 \text{Fe}^{2+} + 4 \text{H}^+ (aq) + \text{O}_2 (aq) \rightarrow 4 \text{Fe}^{3+} + 2\text{H}_2\text{O} \quad E = +0.46 \text{ V} \quad (4)
\]

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

\[
\text{Fe}^{3+} + 3 \text{OH}^- \rightarrow \text{Fe(OH)}_3 \rightarrow \text{FeOOH} + \text{H}_2\text{O} \quad (5)
\]

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].

\[
4 \text{Fe}^{3+} + 3\text{BH}_4^- + 9\text{H}_2\text{O} \rightarrow 4\text{Fe}^{0} + 3\text{H}_2\text{BO}_3^- + 12\text{H}^+ + 6\text{H}_2 \quad (6)
\]

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 FeCl$_3$·6H$_2$O 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 NaBH$_4$ 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 Fe$^{3+}$ requires only 0.0375 mol of BH$_4^-$. 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.
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 Fe^0 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, ie.,
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.
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.

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.

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REFERENCES