Composition Modification of Iron Oxide Particles Using Activated Carbon for Adsorption of Cooper-Polluted Water From Siak River Water Pekanbaru, Riau

Wirdati Mardhatillah, Erwin Amiruddin, Erman Taer

Physics Education – FMIPA, Universitas Riau
Jl. HR Soebrantas, Km. 12.5, Pekanbaru, 28293, Indonesia
wirdae@gmail.com

Abstract. Modification of magnetite ($Fe_3O_4$) nanoparticles with activated carbon of Pulai leaves has been carried out. Magnetite ($Fe_3O_4$) nanoparticles were synthesized from natural sand of Padang beach West Sumatra and activated carbon was extracted from Pulai leaves. Structural and morphological properties of magnetite nanoparticles were studied using X-Ray Diffractometer (XRD) and Scanning Electron Microscope (SEM) respectively. Elemental composition of the samples was identified using X-Ray Fluorescence Spectroscopy (XRF). The heavy metal (cooper) adsorption was determined using Ultra Violet Visible light Spectroscopy (UV-Vis). The ability of magnetite ($Fe_3O_4$) nanoparticles modified with activated carbon for adsorbing the cooper ion in Siak river water is discussed. The results indicate that magnetite ($Fe_3O_4$) nanoparticles modified with activated carbon of Pulai leaves can absorb heavy metal Cu contained in Siak river water.

1. Introduction
Iron oxide magnetic nanoparticles in particular magnetite ($Fe_3O_4$), hematite ($\alpha$-$Fe_2O_3$) and maghemite ($\gamma$-$Fe_2O_3$) nanoparticles originating from coastal sand are very attractive to researchers nowadays because of their super paramagnetic properties which can be modified in nanometre scale so that their applications become wider. These applications include magnetic data storage media [1,2], magnetic sensors [3], separation of industrial pollutants in water [4], and magnetic resonance imaging [5], for biomedicine and bioengineering, it’s helping to carry drugs magnetically to their destination (drug delivery target) [6]. Magnetic nanoparticles are engineered particles in which their magnetic properties can be regulated by using an external magnetic field. In its application these magnetic nanoparticles must have a uniform morphology and have a high magnetization value.

Magnetic nanoparticles can be synthesized in many ways. Some of them are co-precipitation method [7], hydrothermal method [8], sol gel method [9], wet chemical reduction method [10] and Ball milling method [11,12]. Ball milling is a tool used to destroy material using colliding iron balls, the process can make the material in ball milling become smaller. The parameters in this ball milling method are the time and size of the ball milling and the rotating speed of the milling tube. This method is easier, more efficient and cheaper than other methods.

Heavy metal is a material that is often found in nature. Some heavy metals are very useful for living organisms in certain amounts, but can be toxic if the amount is excessive. Heavy metals that are absorbed by the body in excessive amounts can damage the liver, kidneys and lungs. Heavy metals pollution is becoming one of the most serious environment problems globally [13,14]. The heavy metal can pollute water. Therefore, it is very important to remove these heavy metals from wastewater before releasing them into the body of the water such as river or lake. Water pollution...
originates from the disposal of industrial waste. Water that has been polluted if used for daily use is very dangerous. To reduce the concentration of pollutants in water can be done by filtering, ion exchange and absorption[15]. The absorption process is commonly used as a reduction in the concentration of heavy metals in water. This research will use a combination of activated carbon made from Pulai leaves and Fe₃O₄ as an absorber of Cu in the waters.

2. Methodology

2.1. Synthesis of iron oxide particles (Fe₃O₄)
Iron oxide (Fe₃O₄) particles were synthesized from Padang beach sand, West Sumatra using ball milling method. The sand was processed using Iron Sand Separator (ISS) for separating magnetic and non-magnetic particles. After being separated, the samples were then milled for 30 hours and 60 hours to obtain a smaller size of magnetic particle. The magnetic and nonmagnetic particles of ball milling product were separated using NdFeB magnets.

2.2. Preparation of activated carbon of Pulai leaves
The activated carbon used in this experiment was made from Pulai leaves. Pulai leaves were dried first in the sun until they were completely dry. The dried leaves were put into a sample drying oven for 2 days. After drying in the oven then the Pulai leaves were pre-carbonized at 250 °C. The pre-carbonization product was crushed using mortar to form carbon powder. The carbon powder was then pulverized with Ball milling for 20 hours. The fine carbon powder has been activated by activating ZnCl₂. The ratio of carbon powder to activator was 1:1, then dried and neutralized repeatedly until the pH of the washing water was neutral. The carbon powder was then carbonized in N₂ gas.

2.3. Contaminated water samples
The water used in this study is water from the Siak River in Pekanbaru, Riau, Indonesia.

2.4. Copper heavy metal adsorption procedure
Iron oxide (Fe₃O₄) magnetic particles and activated carbon powder were used as absorption of heavy metal Copper (Cu) contained in the Pekanbaru Riau Siak river water. The mixture was divided into three variations, namely, 0.8 gr active carbon leaves Pulai + 0.075 gr Fe₃O₄, 0.8 grams active carbon Pulai leaves + 0.1 gr Fe₃O₄, and 0.8 gr active carbon leaves Pulai + 0.015 gr Fe₃O₄. The mixture that has been varied is immersed in Siak Pekanbaru Riau river water for 2 hours. 200 ml of water was used for each sample mixture. After soaking for 2 hours, the concentration of Cu in the water was measured using UV-Vis.

3. Results and Discussion

3.1. Identification of sample composition using XRF
Identification of the composition of Padang beach sand, West Sumatra was done using the X-Ray Fluorescence spectroscopy (XRF) method. The use of the X-Ray Fluorescence method in this study is based on the consideration that this technique has a detection limit of up to parts per million (ppm) units. In this research two identification stages were carried out, namely identification of the composition before and after being separated between magnetic and non-magnetic particles using Niodium Iron Boron (NdFeB). The result of identification of element contents is shown in Figure 1.
Figure 1. Elemental composition of Padang beach sand, West Sumatra before and after ball milling.

Figure 1 shows the elemental composition of Padang beach sand before and after Ball milling for 60 hours. Before ball milling the composition of sample consists of some elements such as Mg, Al, Si, Ca, Ti, and Fe. After synthesized the sample using ball milling method for 60 hrs, the concentration of Fe and Ti increase from 40.90 to 66.85 % and 7.25% to 9.76% respectively. The non magnetic elements such as magnesium, silicon, aluminum and calcium are decrease in composition. This indicates that Padang beach sand grains break into smaller grains so that the magnetic grains and non-magnetic grains were separated during ball milling process. Moreover, this result shows that Fe and Ti elements cannot be broken down until 60 hours milling process suggesting that Fe and Ti elements to form compounds in the form of FeTiO$_3$ as indicates in X-ray diffraction (XRD) patterns shown by previous researchers [16].

3.2. Morphology of iron oxide particles

The particle shape and size of the beach sand can be seen in Figure 2. Figure 2a shows the results of the Scanning Electron Microscope (SEM) of beach sand that is in Ball milling for 30 hours. The shape of the particles is irregular, the size of each particle also varies. Figure 2b shows the SEM results of beach sand that have been milled for 60 hours. The shape and size of the particles is much smaller than the beach sand which is milled for 30 hours. Ball milling process for a longer time can make iron oxide particle size smaller and have almost the same size.

Figure 2. Scanning electron microscope (SEM) images of iron oxide particles synthesized by ball milling for (a) 30 hours (b) 60 hours.

3.3. Effect of the amount of iron oxide particles to remove copper (Cu) ions

This research uses activated carbon powder made from Pulai leaves, then combined with iron oxide nanoparticles (Fe$_3$O$_4$) synthesized from Padang beach sand, West Sumatra using ball milling method
These nanoparticles were tested for the adsorption of heavy metals such as copper ions in Siak river water. Nanoparticles adsorbents were made in three variations that are sample A with 0.8 gr active carbon concentration mixed with 0.075 gr Fe₃O₄, sample B with 0.8 gr active carbon concentration mixed with 0.1 Fe₃O₄ and C sample with 0.8 gr active carbon concentration mixed with 0.15 gr Fe₃O₄, activated carbon and iron sand were glued using (PVA). The amount of Cu ions adsorption by the sample is shown in Figure 3. Each sample was immersed in Siak river water for two (2) hours. Sample B shows a little adsorption of Cu as much as 9%, sample B absorbs more Cu which is 42%, while sample D absorbs more heavy metal Cu which is 70%. From Figure 3, it shows increasing amount of magnetic iron oxide Fe₃O₄, resulting increase in the removal of cooper ions in the water of Siak River.

![Graph of heavy metals Copper (Cu) removal from the water of the Siak River Pekanbaru Riau.](image)

### 4. Conclusion

The magnetic iron oxide Fe₃O₄ nanoparticles have been synthesized using the Ball milling method and their morphology and composition are studied by using the respective instruments are scanning electron microscopy (SEM) and x-ray fluorescence (XRF). This particle was modified with activated carbon from Pulai leaves to be used to absorb heavy metal Copper (Cu) in the Siak River Pekanbaru water. Modification of Fe₃O₄ iron oxide particles with activated carbon Pulai leaves showed a good capacity in the absorption of heavy metals Copper in the Siak River Pekanbaru water. The amount of heavy metal copper absorbed in the Siak river water increases with the addition of iron oxide Fe₃O₄ particles for a fixed amount of activated carbon, 0.8 grams.

### Acknowledgments

The author thanks the Instrumentation and Magnetism Laboratory staffs and Material Laboratory Riau University for their assistance in making samples and Mr. Tarmizi at Chemistry laboratory UNP Padang for his assistance in analyzing samples using XRF. Thank you also to the Material Laboratory staff at the Andalas University of Padang Faculty of Engineering for their assistance in using SEM facilities.

### References

[1] Erwin 2017 Magnetic interaction intensity in cobalt samarium thin films fabricated using DC magnetron sputtering *AIP Conf. Proc.*: The 6th Int. Conf. Theor. Appl. Phys **1801** 1–6

[2] Black C T, Murray C B, Sandstrom R L and Sun S 2000 Spin-dependent tunneling in self-assembled cobalt-nanocrystal superlattices *Science* **290**(5494) 1131–4

[3] Zeng H, Li J, Liu J P, Wang Z L and Sun S H 2002 Exchange-coupled nanocomposite magnets by nanoparticle self-assembly *Nature* **420** 395–8
[4] Asuha S, Gao Y W, Deligeer W, Yu M, Suyala B and Zhao S 2011 Adsorptive removal of methyl orange using mesoporous maghemite J. Porous Mater 18 581–7
[5] Zhang S, Qi Y Y, Yang H, Gong M F, Zhang D and Zou L G 2013 Optimization of the composition of bimetallic core/shell Fe3O4/Au nanoparticles for MRI/CT dual-mode imaging J. Nanopart. Res 15(2023) 1–9
[6] Morteza M, Shilpa S, Ben W, Sophie L and Tapas S 2011 Superparamagnetic iron oxide nanoparticles (SPIIONS): Development, surface modification and applications in chemotherapy Advan. Drug Delivery Rev (6) 24–46
[7] Khalil M I 2015 Co-precipitation in aqueous solution synthesis of magnetite nanoparticles using iron (III) salts as precursor Arabian J. Chem 8 279–84
[8] Saragi T, Santika A S, Permana B, Syakir N, Kartawidjaja M and Risdiana 2017 Synthesis and properties of iron oxide particles prepared by hydrothermal method IOP Conf. Ser.: Mater. Sci. Eng 196 1–4
[9] Sanpo N, Wen C, Berndt C C and James W 2013 Antibacterial properties of spinel ferrite nanoparticles Formatek 239–50
[10] Chaki H H, Malek T J, Chaudry M D, Tsilor J P and Deshpande M P 2015 Magnetite Fe3O4 nanoparticles synthesis by wet chemical reduction and their characterization Advan. Nat. Sci.: Nanosci. Nanotechnol 6 1–6
[11] Erwin A and Adhy P 2019 The synthesis of magnetic nanoparticles from natural iron sand of Kata beach Pariaman West Sumatera using ball milling method as environmental material MATEC Web of Conf 276 1–5
[12] Erwin A, Salomo S, Adhy P, Utari N, Ayu W, Wita N and Nani S 2020 Magnetic iron oxide particles (Fe3O4) fabricated by ball milling for improving the environmental quality IOP Conf. Ser.: Mater. Sci. Eng 845 012051 1–8
[13] Fujita M, Lde Y and Sato D 2014 Heavy metal contamination of coastal lagoon sediments: fongafale islet, Funafuti atoll, tuvalu Chemosphere 95 628–634
[14] Naser H A 2013 Assessment and management of heavy metal pollution in the marine environment of the Arabian Gulf Mar. Pollut. Bull 72(1) 6–13
[15] Fu F and Wang Q 2011 Removal of heavy metal ions from wastewaters J. Environ. Manage 92(3) 407–18
[16] Erwin A, Amir A, Meilan S, Azura R and Tissa S 2020 Morphology and structural properties of undoped and cobalt doped magnetic iron oxide particles for improving the environmental quality Int. J. Eng. Advan. Technol 9(6) 18–21