Coating of iron sand magnetic material with aminobenzimidazole modified silica via green process

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Abstract. It has been conducted magnetic material coating of iron sand with aminobenzimidazole through a sol-gel process. The magnetic material of iron sand is separated using an external magnet, then it is washed using aquades and Hydrogen Florida solution (HF) 10%. MM-Silica-Aminobenzimidazole (MMSABI) is characterized using a spectrophotometer Fourier Transform Infrared (FTIR), X-ray diffractometer (XRD), and Vibrating Sample Magnetometer (VSM). Moreover, it has been conducted pH acid test (1-6) to the stability by measuring dissolved ion Fe using Atomic Absorption Spectrophotometer (SSA) and the measurement of pH Point Zero Charge (pH\textsubscript{PZC}). The research result shows that the coating process of MMSABI through the successful sol-gel process. Additionally, the aminobenzimidazol cluster enables specific interaction with metal iron with wastewater.

1. Introduction
The magnetic material can be obtained from the synthesis processor iron sand. Iron sand from South Sea Bantul, Yogyakarta consists of mineral that is dominated by oxide iron such as magnetite (Fe\textsubscript{3}O\textsubscript{4}) and Fe\textsubscript{2}O\textsubscript{3} [1]. Intensive research towards magnetite and maghemite (\(\gamma\text{-Fe}_2\text{O}_3\)) in several fields especially environmental or biological fields that have been conducted [2]. The Fe\textsubscript{3}O\textsubscript{4} based material is effective as metal ion adsorbent in water, waste, or slurry because it can be separated from matrix fast using external magnetic field [3]. It depends on the size of the particle, Fe\textsubscript{3}O\textsubscript{4} shows the surface measurement towards the high volume; it means that the surface can be modified to increase the metal adsorption capacity [4]. However, uncoated nanoparticle magnetics easy to oxidize due to the air and is vulnerable in the acidic atmosphere [5].

The magnetic material can be protected through coating using some materials like surfactant, silica, organic polymer, etc [6]. Coating using silica has unique characteristics regarding high biocompatibility, adsorption capacity, and is not soluble in some solvent, and its chemical and heat stability [7]. This process makes the surface of the magnetic material looks like silica (silica-like surface) so that it can be modified with various clusters of organic and inorganic function based on the desired purposes [8]. Based on the literary study, silica coating on the magnetic material of iron sand is still rarely conducted.

Silica-coated magnetite modification is performed in two steps, that is, silica coating on the magnetite and silica functionalization coating magnetite [9]. Magnetite coating with silica from silicate sodium and acid adding no more than a hydrolysis step to obtain gel [4], [9]. According to other researchers report, silica coating on Fe\textsubscript{3}O\textsubscript{4} based on Fe-O-Si bond [4], [7], [10]. Functionalization
of function cluster on silica is made of a siloxane bond (Si-O-Si) between cluster silanol (Si-OH) with the organosilane compound. Function cluster of non-organosilane must be reacted first with an organosilane compound as reported by [11]. Non-organosilane cluster, 2-mercaptobenzimidazole (MBI) is reacted first with 3-chloropropyltrimethoxysilane (CPTS), and then with silica showing the number of dependent MBI more than the reverse procedure [11].

In this publication, it has been reported that magnetic material synthesis of silica-amino benzimidazole was conducted through a sol-gel method in environmental temperature. The successful of the synthesis process is evaluated from a characterization result. Moreover, stability test on pH of acid and pH_{PZC} is conducted.

2. Material and Method

2.1. Materials
Iron sand from Bugel beach, KulonProgo, Yogyakarta, Indonesia. Hydrogen Florida 10% solution, Na_{2}SiO_{3} 11.06 M (26% SiO_{2}) solution, 2-aminobenzimidazole (ABI), and 3 chloropropyltrimethoxysilane (CPTS), N,N Dimethylformamide (DMF) solution, HCl, and NaOH from Merck without specific treatment. Aquades was bought from Chemical Laboratory of Basic FMIPA UGM.

2.2. Instrument
External magnetic (Neodymium, grade N35, size 40 mm x 30 mm x 10 mm), oven (Memmert), grinder, pH-meter, and glass used as in separation and preparation of magnetic material. The analysis of magnetic material composition uses X-Ray Fluorescence (pAnalyticalMinipal 4). Characterization uses diffractrometer X-Ray (Rigaku Multiflex) and Spektrofotometer Fourier Transform Infrared (Shimadzu FTIR – PRESTIGE 21) to identify the structure and functional cluster. The magnetic character uses Vibrating Sample Magnetometer (VSM Oxford 1,2 T). The analysis of the number of ion Fe instability test filtrate uses Atomic Absorption Spectrophotometer (Analytic Jena controlAA 300).

2.3. Procedure

2.3.1. Separation and Preparation of Magnetic Material. Magnetic material (MM) is separated from 100 g of iron sand using external magnetic. BM was crushed until 200 meshes, and then it was washed with HF 10% solution. After having treatment with HF 10% solution, MM was dried in 70-80°C for 4 hours.

2.3.2. Synthesis and Characterization. Synthesis process was performed using two separated container. Container (a) was added by 0.5 gram of MM, 1 ml of HCl 1 M, and 1 ml of Na_{2}SiO_{3} being stirred. Container (b) was added by 1.277 g of ABI compound, 6 ml of N,N Dimethylformamide solution, 1,8 ml CPTS, and 1 ml triethylamine. The mixture (b) was poured into (a) and then stirred while dropped with HCl 1 M until it becomes a gel. MM-silica-Aminobenzimidazole (MMSABI) a gel was stored in a closed container for 1 night and then washed with aquades, and dried in 60°C for 24 hours. MMSABI material was characterized using FTIR, XRD, and VSM.

2.3.3. Measurement pH point of zero charges (pH_{PZC}). 10 mg of MMSABI was put into NaCl 0,001M solution of which pH is conditioned in a range of 1-10. The mixture was shaken out for 60 minutes, and then the adsorbent is separated from the filtrate using external magnetic and the filtrate is filtered. The number of Fe filtrate is analyzed using Atomic Absorption Spectrophotometer.
3. Results and Discussion

3.1. Characteristics of MMSABI

3.1.1. Functional group. Characterization using FTIR is used to verify the existence of silica coating magnetic material and a functional cluster of 2-aminobenzimidazol bound to silica. Spectra FTIR of MM, MM-Silika (MMS), standard 2-aminobenzimidazol (ABI), and MMSABI is presented in figure 1.

![Figure 1. Spectra IR of (a) BM, (b) BMS, (c) ABI, and (d) MMSABI](image)

The existence of silica on the surface of the magnetic material is indicated by the occurrence of absorption bands on standard 2-aminobenzimidazol which also occurs on MMSABI. The absorption band on BM is 1635 and 3488 cm\(^{-1}\) vibration -OH of Si-OH or Fe-OH, stretching vibration Si-O of silanol on 941 cm\(^{-1}\), and 570 cm\(^{-1}\) is stretching vibration Fe-O of Fe\(_3\)O\(_4\). The coating of the MM surface with silica (MMS) is shown on the bending vibration Si-O-Si on 470 and 1087 cm\(^{-1}\). The existence of 2-aminobenzimidazol cluster on MMSABI compared to spectra ABI is shown on the existence of stretching vibration bands C=C of aromatic benzene rings on 1481 cm\(^{-1}\) and stretching vibration C=N of imidazole rings on 1558 cm\(^{-1}\). It is strengthened by stretching vibration C-H on tetrahedral carbon on 2954 cm\(^{-1}\) from 3-clopropyltrimethoxysilane compound (CPTS). Bending vibration N-H is about 1560 cm\(^{-1}\) and 3300 cm\(^{-1}\), and possibly overlap with vibration C=N of imidazole rings and vibration –OH so that the form of absorption bands is widened [9], [12]

3.1.2. Structure. The peak of diffraction of silica occurs on 2\( \theta \) = 17.8°; 19.1°; and 20.6° [13]. Diffractogram XRD of MMSABI in Figure 2 (b) shows the widened peak on 2\( \theta \) = 20° - 23° indicating the existence of silica, and it means that the silica has coated magnetic material.
Moreover, the structure of the silica coating magnetic material is supposed to have an amorphous structure [14]. The decreased altitude and intensity of the diffraction peak, especially index [311] on MMSABI compared to MM based on table 1, indicating that magnetic material coated by non-magnetic material (silica and aminobenzimidazol). Based on figure 2 and table 1, diffraction peak for index [311] shows that value 2θ is unchanged. It means that the coating process does not change the crystal structure of MM; it decreases the altitude and intensity of the diffraction peak instead [4].

![Figure 2. Diffract gram XRD of (a) Magnetic Material (MM) and (b) MMSABI](image)

**Table 1. Parameters of [311] peak from XRD pattern**

| Material   | 2θ  | Altitude | Intensity |
|------------|-----|----------|-----------|
| MM         | 35.39 | 409     | 609       |
| MMSABI     | 35.46 | 341     | 391       |

3.1.3. Magnetic properties. The presence of nonmagnetic materials such as silica and ABI can affect the magnetic properties of the MM itself. The measurement of the magnetic properties of MM and MMSABI with VSM gives the hysteric curve as in figure 3. The hysteresis curve shows the amount of energy required for magnetization. According to figure 3, the form of the hysteresis loop is very small for MM and MMSABI, which means low magnetization energy so that it belongs to the soft magnetic category. This assumption is reinforced by He ≠ 0 for MM and MMSABI (Table 2) and this indicates that both are ferromagnetic [4]. The decrease of magnetization energy after magnetic material coated with nonmagnetic materials was also reported by [9], [15].
**Figure 3.** VSM hysteresis curve of (a) MM dan (b) MMSABI

The parameter of the magnetic feature measured includes the saturation field ($M_s$), coercive field ($H_c$), and permanent magnetization field ($M_r$). $M_s$ value shows external magnetic strength given to inducted magnetic material in the sample, $M_r$ is the magnitude of magnetic field that still has sample after the external magnet is removed, and $H_c$ is the magnitude of magnetic field given in opposite direction to remove $M_r$. Based on the parameter calculation presented on Table 2, especially $M_r$ value, the characteristic of MMSABI is lower than MM or silica coated MM (MMS). It happens due to the existence of non-magnetic material, which is silica and aminobenzimidazol coating the surface of the magnetic material so that it decreases the magnetic feature of the magnetic material.

**Table 2.** Parameters of magnetic material properties

| Material  | $M_s$ (emu/g) | $M_r$ (emu/g) | $H_c$ ($\times 10^{-2}$ T) |
|-----------|--------------|--------------|--------------------------|
| MM        | 44.90        | 10.90        | 1.69                     |
| MMS [15]  | 38.231       | 4.535        | 1.93                     |
| MMSABI    | 23.30        | 5.41         | 1.93                     |

3.2. Stability of Adsorbent
The stability of the adsorbent is necessary to be known to support its application because the metal ion adsorption in solution is influenced by pH. Magnetic-material-based adsorption material is very susceptible to discharged / dissolved in acid solution. Therefore, if it happens, the separation of adsorbent from the matrix is difficult. The stability test of MMBSI is evaluated based on the amount of ion Fe dissolved in acid condition (pH 1-6). The percentage calculation of ion Fe dissolved is presented in figure 4.

**Figure 4.** Percentage of Fe dissolved from MMSABI
The amount of ion Fe dissolved at pH 1 is higher than pH 2-6, but there is no significant difference. In high acid condition (pH 1), aminobenzimidazol is dissolved, so the proton interaction (H⁺) with silica is more effective to create silica ion (Si-O⁻) dissolved, and it cut Fe-O-Si bound. MM surface that has not been covered by silica and aminobenzimidazol makes ion Fe dissolved when contacting with an acid solution, in pH 2 – 6, the coating material of MM prevent protonation of amina cluster and causes low solubility [15].

3.3. Measurement of pH Point Zero Charge (pH<sub>PZC</sub>)

pH Point Zero Charge (pH<sub>PZC</sub>) is certain pH when the surface is neutral, and pH<sub>PZC</sub> is the intersection point of the initial and final pH curves [16]. The obtained pH<sub>PZC</sub> can be used to identify the surface load of adsorbent before and after the value. pH<sub>PZC</sub> value of MMSABI of 5.398 is obtained from the curve from the intersection of the initial and final pH curve as presented in figure 5. The result means that MMSABI surface has a positive partial load on pH solution <5.39, while when pH solution >5.39, its load is negative. In pH solution range of 5.39, the value of final pH is higher than the initial pH, meaning that ion H⁺ in the solution is decreased and tends to be in the adsorbent surface. It creates protonation of am cluster, so that MMSABI surface will have a positive partial load. In the range of pH solution > 5.39, there will be the adverse result.

4. Conclusion

This research shows that synthesis of magnetic material of silica-coated sand modified with aminobensimidazol using sol-gel method is successfully conducted. The procedure is easy and environmental friendly because it does not need many chemical reagents and extreme condition. Besides obtaining stable adsorbent, the existence of amino cluster makes it potential to be used in separation and adsorbent process of the metal ion. Therefore, MMSABI adsorbent needs to be tested to know the performance.

References
[1] H. Putra, I. Satyarno, A. B. Wijatna, and I. Satyarno, 2008, Penggunaan Pasir Besi Dari Kulon Progo Dengan Berat Jenis 4 , 311 Untuk Mortar Perisai, Forum Tek. Sipil, XVIII, 909–920.
[2] G. Giakisikli and A. N. Anthemidis, 2013, Analytica Chimica Acta Magnetic materials as sorbents for metal / metalloid preconcentration and / or separation . A review, Anal. Chim. Acta, 789, 1–16.
[3] W. Yantasee, C. L. Warner, T. Sangvanich, R. S. Addleman, T. G. Carter, R. J. Wiacek, G. E. Fryxell, C. Timchalk, and M. G. Warner, 2007, Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles, Environ. Sci. Technol., 41 (14), 5114–5119.
[4] N. Nuryono, N. M. Rosiati, B. Rusdiarso, S. C. W. Sakti, and S. Tanaka, 2014, Coating of magnetite with mercapto modified rice hull ash silica in a one-pot process, *Springerplus*, 3 (1), 515.

[5] M. Mahmoudi, S. Sant, B. Wang, S. Laurent, and T. Sen, 2011, Superparamagnetic iron oxide nanoparticles (SPIONs): Development, surface modification and applications in chemotherapy, *Adv. Drug Deliv. Rev.*, 63 (1–2), 24–46.

[6] M. Faraji, Y. Yamin, and M. Rezaee, 2010, Iranian chemical society magnetic nanoparticles: synthesis, stabilization, functionalization, characterization, and applications, *J. Iran. Chem. Soc.*, 7 (1), 1–37.

[7] D. Yang, J. Hu, and S. Fu, 2009 Controlled Synthesis of Magnetite-Silica Nanocomposites via a Seeded Sol-Gel Approach, *J. Phys. Chem. C*, 113, 7646–7651.

[8] P. K. Jal, S. Patel, and B. Mishra, 2004 Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions, *Talanta*, 62 (5), 1005–1028.

[9] Y. Lin, H. Chen, K. Lin, B. Chen, and C. Chiou, 2011 Application of magnetic particles modified with amino groups to adsorb copper ions in aqueous solution, *J. Environ. Sci.*, 23 (1), 44–50.

[10] C. Huang and B. Hu, 2008 Silica-coated magnetic nanoparticles modified with γ-mercaptopropyltrimethoxysilane for fast and selective solid phase extraction of trace amounts of Cd, Cu, Hg, and Pb in environmental and biological samples prior to their determination by inductively coupled plasma optical emission spectrometer, *Spectrochim. Acta Part B*, 63, 437–444.

[11] E. F. C. Alcantara, E. A. Faria, D. V. Rodrigues, S. M. Evangelista, E. DeOliveira, L. F. Zara, D. Rabelo, and A. G. S. Prado, 2007 Modification of silica gel by attachment of 2-mercaptobenzimidazole for use in removing Hg(II) from aqueous media: A thermodynamic approach, *J. Colloid Interface Sci.*, 311 (1), 1–7.

[12] R. Abraham and K. K. M. Yusuff, 2003 Copper(II) complexes of embelin and 2-aminobenzimidazole encapsulated in zeolite Y-potential as catalysts for reduction of dioxygen, *J. Mol. Catal. A Chem.*, 198 (1–2), 175–183.

[13] P. Dhawade and R. Jagtap, 2012 Comparative Study of Physical and Thermal Properties of Chitosan-Silica Hybrid Coatings Prepared by Sol-Gel Method, *Der Chem. Sin.*, 3 (3), 589–601.

[14] U. Kalapathy, a. Proctor, and J. Shultz, 2002 An improved method for production of silica from rice hull ash, *Bioresour. Technol.*, 85 (3), 285–289.

[15] Muflikhah, B. Rusdiarso, E. G. R. Putra, and Nuryono, 2017 Modification of Silica Coated on Iron Sand Magnetic Material with Chitosan for Adsorption of Au (III), *Indo. J. Chem.*, 17 (2), 264–273.

[16] S. H. Dewi and Ridwan, 2012 Sintesis dan karakterisasi Nanopartikel Fe3O4 Magnetik Untuk Adsorpsi Kromium Heksavalen,” *Indones. J. Mater. Sci.*, 13 (2), 136–140.