Adsorption of Fe\(^{3+}\) ion from Aqueous Solution onto Rice Husk Biocomposite Magnetic Nanoparticle

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Abstract. Rice husk (RH), an agricultural waste, is abundantly available in South Kalimantan. RH has been recycled only for low-value application, although rice husk has the potential to be used as natural fiber. The aim of this research is to produce an adsorbent based on rice husk fiber (RHF) and magnetic nanoparticles (MNPs) and study its performance on Fe\(^{3+}\) ion adsorption, effect on total suspended solid (TSS) and color adsorption. Rice husk was dried (60 mesh), then run through delignification process to eliminate lignin using 1% of NaOH. Rice husk biocomposite (RHB) was produced using a one-pot solvothermal reaction in the presence of RHF and FeCl\(_3\).6H\(_2\)O. The surface of RHB was modified by amine group (RHB-MH). As control, the RHB without modification was also produced (RHB-M). The optimum adsorption was reached at pH 5 in a 60-minute period and adsorption capacity for RHB-M and RHB-MH reached 47.63 and 52.46 mg/g, respectively. The RHB-MH also had the capability to adsorb TSS and color, where approximately 87.5% of TSS and 85.81% of color were reduced. Regarding its reusability, the RHB-MH showed a good performance in 4 repeated uses. The addition of amine on the biocomposite may have affected the adsorbent by enhancing its adsorption capacity, reduced TSS and color for reactivity toward a wide range of organic pollutant.

1. Introduction
Rice husk is a potential natural fiber as raw material for composite, which contains of 35.68% of fiber. The composite material has many advantages, such as having a light weight and better mechanical properties [1]. Currently, magnetic nanoparticles with dimension in nanometers are a very interesting object to research in several applications in industry and in the development of science and technology. Magnetic nanoparticles have been widely used in several fields of research such as magnetic storage [2], immunoassay [3], and as an adsorbent [4, 5]. Syntheses of magnetic nanoparticles (MNPs) by solvothermal method produce nanoparticles that are stable, uniform particle size and good magnetisation property [5, 6]. There has been investigations about metal ion removal for waste water treatment technique including chemical precipitation, filtration, ion exchange, membrane and adsorption [7-9]. An adsorption process will be effective with a high metal adsorption capacity. In order to make the process greener, it is possible to use rice husk fibre as raw material for biocomposite magnetic nanoparticle with its capability to be developed as adsorbent. The biocomposite magnetic nanoparticle which used rice husk fibre has not been studied; it is an interesting topic to focus on and for further studies.

Regarding its application, an adsorbent is used to adsorb metal ions which are contaminants in hazardous and toxic wastewater or water containing contaminants. In this study, it is especially applied
in the treatment of iron (Fe), a type of heavy metal which is less toxic and, at the right amount, is essential for the body. However, excess or accumulated Fe metal ions occurring over a long period of time can be dangerous and toxic [4]. Previous research has shown the capability of biocomposite with magnetic nanoparticles as a modified adsorbent for the removal of ion, lead and arsenate [5, 10]. In addition, the amine modification on the surface of biocomposite has an effect in the reduction of TSS and color, due to protonation and dissociation of adsorbent and ion in aqueous solution. Rice husk, which is an abundant agricultural waste, can be used as a source of fibre in the preparation of biocomposite magnetic nanoparticles. This research focused on the effect of pH on Fe$^{3+}$ ion adsorption capacity and TSS and color reduction intensity in aqueous solution. This research is expected to increase the usability value of rice husk and overcome the problem of wastewater/liquid that is harmful to the environment.

2. Materials and Method

2.1. Materials

The main material used in these experiments is native rice husk obtained from a rice mill in Martapura, South Kalimantan; liquid waste of Sasirangan industry taken from “Kampong Sasirangan” Banjarmasin, South Kalimantan. Other materials including ethylene glycol (C$_6$H$_{12}$O$_2$), sodium acetate anhydride (C$_2$H$_3$NaO$_2$), iron(III) chloride hexahydrate (FeCl$_3$.6H$_2$O), 1,6-hexanediamine (HMDA), sodium hydroxide (NaOH), hydrochloric acid (HCl), and ethanol (C$_2$H$_5$OH) were purchased from Sigma Aldrich without further purification.

2.2. Preparation of rice husk fibre

RH was blended continuously with 60 mesh sieve and run through delignification. 40% of the RH was soaked for 2 hours in a solution of 1% NaOH (ASTM 1109-56), then heated at 80°C while stirred 150 rpm for 2 h, then washed until the filtrate was neutral and dried (RHD) at 80°C for 24 h.

2.3. Preparation of biocomposite magnetic nanoparticle

Biocomposite was produced by one-step solvothermal method in the presence of ethylene glycol (24 ml), sodium acetate anhydride (1.8 g), and iron (III) chloride hexahydrate (0.8 g), then heated at 80°C while stirred. Next, 1,6-hexanediamine (7 mL) and RHD (5 g) were added to the solution and poured to a Teflon stainless steel autoclave, then kept in an oven at 200°C for 6 h. The resulting products are called BRH-MH (with 1,6-hexanediamine) and BRH-M (without 1,6-hexanediamine) and kept in DI water for further use.

2.4. Adsorption of Fe$^{3+}$ ion onto biocomposite magnetic nanoparticle

The adsorption of Fe$^{3+}$ ion was conducted in 15, 30, 60, 120, and 240 min and at various pH levels (5, 6, 7, 8) using BRH-MH and BRH-M as an adsorbent in batch processes. Briefly, a certain amount of adsorbent was placed into a 500 ml bottle, the wastewater solution containing 40 ppm of Fe$^{3+}$ ion was added and the adsorption process was performed under a shaking rate of 150 rpm.

2.5. Characterization

Components in the sample were detected by Field-Emission Scanning Electron Microscopy (FE-SEM, JOEL JSM-6500F) with energy-dispersive X-ray spectroscopy (EDAX) for surface morphology observation. The crystallization of sample was performed on X-ray diffraction (XRD), Rigaku D/MAX-B X-ray diffractometer by using Cooper K-alpha (Cu Kα) radiation with 2θ in the range of 10 to 40 °C at a scan rate of 2° min$^{-1}$. The operation voltage and current were kept at 40 kV and 100 mA, respectively. XRD analysis is an analysis to determine the crystal structure. Crystalline Index was calculated by the equation:

$$CRI = \frac{(I_{002}-I_{am})}{I_{002}}$$ (1)
Where $I_{cr}$ is the intensity of the crystalline of a cellulose (22.6°) and $I_{am}$ is the intensity of the amorph part of cellulose (16.2°).

2.6. Analysis
The remaining Fe$^{3+}$ ion in solution was analyzed by Inductively Coupled Plasma (ICP) (Activa S ICP Optical Emission Spectrometer) after separating it from the adsorbent. TSS was measured by ASTM D 5907-09 Standard Test Method for Filterable and Non Filterable Matter in water. Sample (50 ml) was filtered with filter paper that had been weighed, and then put in an oven for 1 hour at 80 °C. After that it was cooled in a desiccator and weighed, until a constant weight was obtained. To obtain estimates of TSS, the difference between the total dissolved solids and total solids calculated by the following formula:

$$TSS = \frac{(A-B)}{V}$$  (2)

Where:

- $TSS$ = Total Suspended Solid (%)
- $A$ = weight of filter paper + dry residue (mg)
- $B$ = weight of filter paper (mg)
- $V$ = sample volume (ml)

For the measurement of the color reduction intensity, a UV-Vis spectrophotometer was used, and the drop in color absorbance value was measured by the following formula:

$$\text{Color reduction} = \frac{(C-D)\times 100\%}{C}$$  (3)

Where:

- $C$ = absorbance at the initial condition
- $D$ = absorbance after adsorption

The wavelength during spectrophotometer observation for original waste was the same as that used to measure liquid after adsorption.

3. Results and Discussion

3.1. The adsorption of Fe$^{3+}$ ion onto biocomposite magnetic nanoparticle
MNPs growth in situ of the RHF was confirmed by EDAX and XRD. After delignification, the crystallinity index (CrI) of RH was increased about 16.77% and silica content reduced about 78%. The magnetic nanoparticle was formed on the surface of RHF with diameter size 30–50 nm. The resulting biocomposite magnetic nanoparticle is the same with our previous study [11]. The adsorption process was carried out using a shaker with variation of contact time i.e. 15, 30, 60, 120 and 240 minutes (Figure 1). The observation of contact time was done to obtain the optimum time for the adsorption using RHB-M and RHB-MH containing Fe$^{3+}$ ion in aqueous solution. From Figure 1, it can be seen that the capability of RHB-M and RHB-MH in binding of Fe$^{3+}$ ion increased during the first 30 min until it reached the optimum adsorption capacity at about 46.31 mg/g and 49.73 mg/g, respectively. The amount of adsorbed Fe$^{3+}$ ion started to be constant at 30 min. This the constant value was due to a saturated condition, where the entire surface of the adsorbent had been filled by Fe$^{3+}$ ion. On this condition, a dynamic equilibrium of adsorption rate occurred, where no Fe$^{3+}$ ion was absorbed nor released or dissolved back into the adsorbate, since it had reached the equilibrium point [12]. RHB-MH had better adsorption capacity, about 7.4% more than that of RHB-M. This may have occurred because the biocomposite magnetic nanoparticle amino group (RHB-MH) had a smaller diameter particle size (50 nm) that could expand its surface area as an adsorbent, with high permeability and
stable mechanical and thermal properties, so that the adsorption process could take place with better results [13].

The adsorption capacity of biocomposites magnetic nanoparticle was influenced by the pH solution, which corresponded to the protonation or deprotonation of the active side surface of the sorbent [14, 15]. Variation of pH would affect the surface load of the adsorbent, the degree of ionization and what species could be absorbed in the adsorption. The pH value could also affect the chemical equilibrium, either on the adsorbate or on the adsorbent. In this pH variation the possibility of chemical bonds between adsorbent and adsorbate might occur. The ability of RHB-M and RHB-MH adsorbents on the absorption of Fe$^{3+}$ ion can be seen in Figure 2.

Figure 2 shows the optimum condition at pH 5 for RHB-M and RHB-MH adsorbent with adsorption capacity about 47.63 mg/g and 52.46 mg/g, respectively. Below pH 5, adsorption was not expected to have a good performance because at low pH the Fe$^{3+}$ ion on magnetic would leach to the solution. The high adsorption capacity occurred at a dynamic equilibrium between the adsorption rate, reaching the equilibrium point. Previous research was carried out on adsorption of Fe$^{3+}$ ion with biocomposite magnetic nanoparticle by using cellulose of purun tikus as fibre source. The Fe$^{3+}$ ion was absorbed for 9 h at pH 7 by BPT-M and BPT-MH, about 16.78 mg/g for and 33.19 mg/g respectively. Based on the results, magnetic biocomposite nanoparticles-based rice husk fibre has approximately 58% greater adsorption capacity than magnetic biocomposite-based purun tikus nanoparticles. This is possibly because of the different sources of fibre used and the different fibre sizes providing different surface areas for the adsorbent, eventually affecting the adsorption capacity.

In order to evaluate the adsorption capacity of biocomposite, delignified rice husk fiber (RHD) as control adsorbent was used in the same condition, and it had an adsorption capacity of 30.72 mg/g. The RHD contains about 40% cellulose, which has –OH as active group that also has the ability to bind Fe$^{3+}$ ion in aqueous solution. The biocomposite magnetic nanoparticle adsorption capacity was 45.6% higher than that of rice hush fibre.

3.2. Effect of total suspended solid and color reduction during adsorption of Fe$^{3+}$ ion onto biocomposite magnetic nanoparticle

The TSS was calculated based on the conditions of adsorption with RHB-M and RHB-MH as adsorbents at pH 5, 6, 7 and 8. Figure 3 show at pH 5, a significant decrease in TSS effectiveness, at
about 67.7% and 87.5% for RHB-M and RHB-MH, respectively. In addition, the optimum degradation of organic and inorganic compounds took place at pH 5, causing the suspended substances to dissolve again in large amounts and decrease the content of TSS.

The wastewater sample used was waste of Sasirangan fabric containing dye, so that the adsorbent also had capability to adsorb color from the solution. Figure 4 shows the effectiveness of dye reduction at various pH of liquid waste. Dye reduction analysis was performed using UV-Vis Spectrophotometer at wavelength (λ) 317 nm. In the color analysis results, color intensity was measured at various pH, and it was found that at pH 5, more dye was adsorbed by RHB-M and RHB-MH, about 44.64% and 85.81% respectively. At the lower pH of the adsorption, the amount of H+ ions on the surface of the adsorbent increased so that the adsorbent surface was positively charged [16, 17], causing an increase in dye adsorption. This was due to the strong interaction of electrostatic attraction between the positive charge on the surface of the adsorbent and the anionic dye molecule [16-18]. The percentage of the effectiveness of dye reduction was higher in the acid solution than in the neutral and alkaline solutions. At acidic pH, more protons would be available to protonate the amine groups into the -NH3+. The increased percentage of the effectiveness of dye reduction was possible due to protonation, which would be the exclusive cause for increased electrostatic attraction between the negatively charged anions in the dye molecules and the positively charged adsorption active sites on the adsorbent [19].

**Figure 3.** Effectiveness of TSS reduction with variation of pH. Reaction condition: 200 mL of sample, 0.05 g adsorbent, stirring at 150 rpm for 60 min

**Figure 4.** Effectiveness of color reduction with variation of pH. Reaction condition: 200 mL of sample, 0.05 g adsorbent, stirring at 150 rpm for 60 min

4. Conclusion

The biocomposite magnetic nanoparticle was successfully prepared by solvothermal method using rice husk fibre. The optimum condition of Fe3+ ion adsorption occurred at pH 5 for 30 min which yielded a high adsorption capacity of 52.46 mg/g and a TSS reduction of about 87.5% for RHB-MH. The color reduction in aqueous solution was approximately 85.81% by RHB-MH. The biocomposite magnetic nanoparticle is a candidate material for the adsorption of metal ion and color/dye in aqueous solution.

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