Adsorption of Fe3+ ion from Aqueous Solution onto Rice Husk Biocomposite Magnetic Nanoparticle

by Doni Wicakso

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Abstract. Rice husk (RH), an agricultural waste, is abundantly available in South Kalimantan. RHs have been recycled only for low-value application, whereas rice husk has potential as natural fiber. The aim of this research is produced adsorbent based on rice husk fiber (RHF) and magnetic nanoparticle (MNPs) and its performance for Fe^{3+} ion adsorption, total suspended solid (TSS) and reducing color intensity. Rice husk was dried (60 mesh), then through delignification process to eliminate lignin by 1% of NaOH. Rice husk biocomposite (RHB) was carried out by one-pot solvothermal reaction in the presence of 1,6 hexanediamine (RHB-MH). The product was produced without 1,6 hexanediamine called RHB-M. The optimum condition of adsorbent was optimum at pH 5 for 60 min. The adsorption capacity of RHB-M and RHB-MH was achieved up to 47.63 and 52.46 mg/g, respectively. Reusability of RHB-MH shows good performance in 4 repeated used. The iron content and amine functionalized on biocomposite may affect the adsorbent by enhancing the high adsorption capacity 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 a light weight and better mechanical properties [1]. Currently, magnetic nanoparticles with nanometer size are very interesting object to be researched 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], and immunoassay [3], and as an adsorbent [4, 5]. Synthesis of magnetic nanoparticles (MNPs) by solvothermal method produces nanoparticles that are stable, uniform particle size and good magnetification property [5, 6]. There has been investigated about metal ion removal for waste water technique including chemical precipitation, filtration, ion exchange, membrane and adsorption [7-9]. Adsorption process will be effective by high adsorption capacity to metal. In order to applied green process, utilization of rice husk fibre as raw material for biocomposite magnetic nanoparticle has capability to develop as adsorbent. The biocomposite magnetic nanoparticle which used rice husk fibre has not been studied; it is interesting to opportunity and the potential material to study.

Application of adsorbent is to adsorb metals which are contaminants in hazardous and toxic waste water or water containing contaminants. Especially in the treatment of iron (Fe), it is a heavy metal type which is less toxic and sufficiently essential for the body, but if excess or accumulation of Fe metal ions occurs over a long period of time it can be dangerous and toxic [4]. Previous research has

shown the capability biocomposites with magnetic nanoparticles as modified adsorbent [5, 10]. 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 was focus on effect of pH to the adsorption Fe^{3+} ion capacity, TSS and reducing color intensity in aqueous solution. In addition, this research is expected to increase the useful value of rice husk and overcome the problem of waste water/liquid that is harmful to the environment.

2. Materials and Method

2.1. Materials
The materials used in this experiment is native rice husk were obtained from rice mill at Martapura, South Kalimantan, liquid waste Sasirangan industry taken from "Kampong Sasirangan" Banjarmasin, South Kalimantan, ethylene glycol ($C_6H_6O_2$), sodium acetate anhydride ($C_2H_3NaO_2$), iron(III) chloride hexahydrate ($FeCl_3.6H_2O$), 1,6-hexanediamine (HMDA), sodium hydroxide (NaOH), hydrochloric acid (HCl), ethanol (C_2H_5OH) are purchased from Sigma Aldrich without further purification.

2.2. Preparation of rice husk fibre
RH was blended the continuous with 60 mesh sieve and through by delignification. The 40% of RH soaked for 2 h in a solution of 1% NaOH (ASTM 1109-56), then heated at 80 °C while stirring 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), iron(III) chloride hexahydrate (0.8 g) then heated at 80 °C under stirred. Next step, the solution was added 1,6-hexanediamine (7 mL), RHD (5 g) and pored to Teflon stainless steel autoclave, then keep in an oven at 200 °C for 6 h. As a control, biocomposite without addition of 1,6-hexanediamine was also produced.

2.4. Adsorption of Fe^{3+} ion onto biocomposite magnetic nanoparticle
Adsorption of Fe^{3+} ion was conducted for 15, 30, 60, 120, and 240 min and adsorption run on function of pH (5, 6, 7, 8) using BRH-MH and BRH-M as an adsorbent in batch process. Briefly, certain number of adsorbent placed in to 500 mL bottle the added waste water solution and adsorption process under 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). The X-ray diffraction (XRD) measurement was performed on Rigaku D/MAX-B X-ray diffractometer by using Cooper K-alpha (Cu Kα) radiation with 2θ in the range from 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 is calculated by the equation:

$$CrI = \frac{(I_{002} - I_{am})}{I_{002}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (1)$$

Where I_{002} is the intensity of the crystalline of a cellulose (22.6°) and intensity I_{am} amorph part of cellulose (16.2°).

2.6. Analysis
The resulting solution of adsorption was analyzed by Inductively Coupled Plasma (ICP) (Activa S ICP Optical Emission Spectrometer) to determine the content of Fe^{3+} ion. TSS calculates 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 the oven for 1 hour at 80 °C. After it is cooled in a desiccators and weighted, until obtain a constant weight. To obtain estimates of TSS, calculated the difference between the total dissolved solids and total solids, by 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)

The calculation of color intensity of dyes used UV-Vis spectrophotometer, the effectiveness of reducing color indicate by dye absorbance value measured by the formula:

$$Dye\ intensity = \frac{(C-D)x\ 100\%}{C}$$ …………….…..………….……….....................…….....(3)

Where:

C = absorbance of the initial conditions
D = adsorption condition of the waste 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 EDX and XRD. After delignification, the crystalinity index (CrI) of RHF was increased about 16.77% and reduced silica content about 78%. The magnetic nanoparticle was formed on the surface of RHF with diameter size 30–50 nm. The resulting biocomposite magnetic nanoparticle is same with our previous study [11]. The adsorption process was carried out using shaker with variation of contact time of 15, 30, 60, 120 and 240 min (Figure 1). The observation of contact time is to obtain the optimum time for adsorption using RHB-M and RHB-MH which 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 from 0 to 30 min until reached optimum adsorption capacity about 46.31 mg/g and 49.73 mg/g, respectively. The adsorbed Fe^{3+} ion start constant at 60 min, the constant value is due to saturated condition on entire surface of the adsorbent has been fulfilled by Fe^{3+} ion. On this condition, was occurs a dynamic equilibrium between adsorption rate, where no Fe^{3+} ion is absorbed or released or dissolved back into the adsorbate, it has reached the equilibrium point [12]. RHB-MH has better adsorption capacity about 7.4% then that RHB-M. This may occur because of the biocomposite magnetic nanoparticle amino group functionalized (RHB-MH) has a smaller diameter particle size (50 nm) that can expand the surface area as a adsorbent, with high permeability and stable mechanical and thermal properties, so that the adsorption process can take place with a better results [13].

The adsorption capacity of biocomposites magnetic nanoparticle is influenced by the pH solution, this corresponds to the protonation or deprotonation of the active side surface of the sorbent [14, 15]. Variation of pH will affect the surface load of the adsorbent, the degree of ionization and what species can be absorbed in the adsorption. The pH value can 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 may 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. The adsorption was occurs a dynamic equilibrium between the adsorption rate or reaching the equilibrium point. Previous research was carried out by adsorption of Fe^{3+} ion with biocomposite magnetic nanoparticle by using "purun

tikus" as fibre source. The Fe^{3+} ion absorbed for 9 h contact time at pH 7 by biocomposite purun tikus without amino group (BPT-M) and biocomposite purun tikus with amino group (BPT-MH) are 16.78 mg/g for and 33.19 mg/g, respectively [16]. Based on results, the magnetic biocomposite nanoparticle-based rice husk fibre has approximately 58% greater adsorption capacity than the magnetic biocomposite-based purun tikus nanoparticle. This may be possible, because the source of the fibre used is different, the different fibre sizes thereby providing different surface areas for the adsorbent and affecting the adsorption capacity.
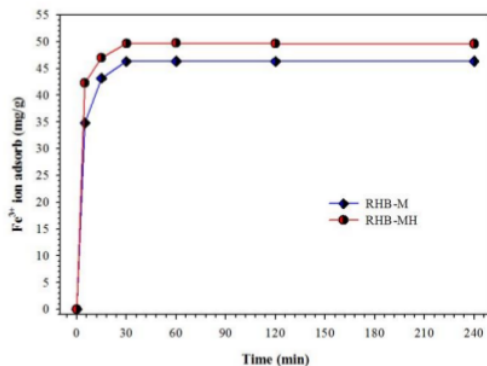
Figure 1. Concentrations of Fe^{3+} ion after adsorption at various contact times by RHB-M and RHB-MH as adsorbent. Reaction conditions: 200 mL of sample, 0.05 g of adsorbent, stirring 150 rpm and pH 5.
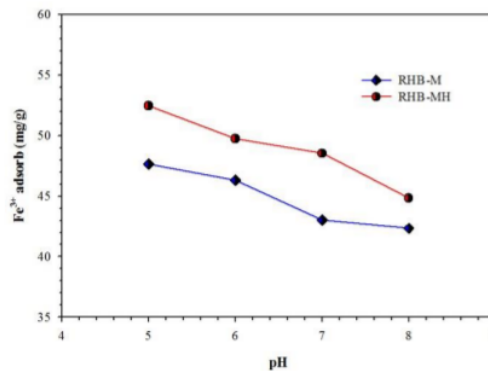
Figure 2. Concentrations of Fe^{3+} ion after adsorption at pH by RHB-M and RHB-MH as adsorbent. Reaction conditions: 200 mL of sample, 0.05 g of adsorbent, stirring 150 rpm for 60 min.

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

3.2. Effect of total suspended solid and reducing color solution
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 decreased in TSS effectiveness about 67.7% and 87.5% for RHB-M and RHB-MH, respectively. In addition, the degradation of organic and inorganic compounds take place optimum at pH 5 causing the suspended substances to dissolve again in large amounts and decrease the content of TSS.

The waste water sample is waste of Sasirangan fabric containing dye, so that the adsorbent also have capability to adsorb color of solution. Figure 4 shows the effectiveness of dye reduction to the pH of liquid waste. Reducing of dye analysis was performed using UV-Vis Spectrophotometer at wavelength (λ) 317 nm. Based on the color analysis results obtained the color intensity at each pH, at pH 5 more dyes adsorbed by RHB-M and RHB-MH about 44.64% and 85.81%, respectively (Figure 5). The lowest pH of the adsorption, amount of H^+ ions in the surface of the adsorbent increases that the adsorbent surface is positively charged [17, 18], causing an increase in dye adsorption. This is due to the strong interaction of electrostatic attraction between the positively charge on the surface of the adsorbent and the anionic dye molecule [17-19]. The percentage of the effectiveness of reduction of the dye is higher in the acid solution than in the neutral and alkaline solutions. At acidic pH, more protons will be available to protonate the amino groups into the -NH^{3+}. The increased percentage of

the effectiveness of reduction of the dye is possible due to protonation, which would be the exclusive cause for increased electrostatic attraction between the negatively charged anions in the dye molecules and positively charged adsorption active sites on the adsorbent [20].
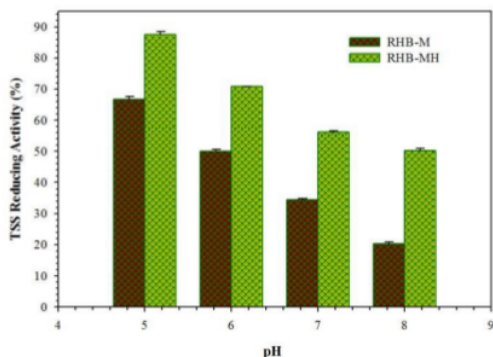

Figure 3. Effectiveness of TSS reduction with variation of pH. Reaction condition: 200 mL of sample, 0.05 g adsorbent, stirring 150 rpm at 60 min
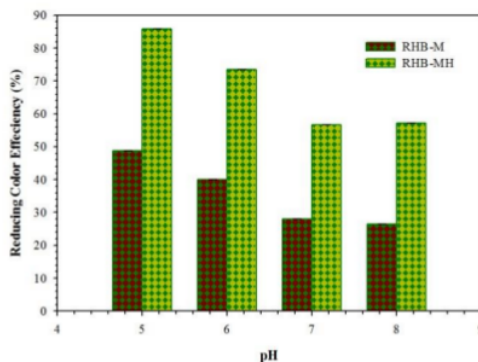
Figure 4. Effectiveness of reducing color with variation of pH. Reaction condition: 200 mL of sample, 0.05 g adsorbent, stirring 150 rpm at 60 min

The reusability of the adsorbent is an important factor in terms of economic aspects as well as being able to reduce secondary waste. One of the advantages of biocomposite is reusability and easily separated between the filtrate and the adsorbent with external magnet field. The adsorbent have been used in the adsorption process, filtered and washed. Then, the recovered adsorbents were used for the next adsorption process. The adsorption ion capacity was calculate to determine the reusability performance of adsorbent.
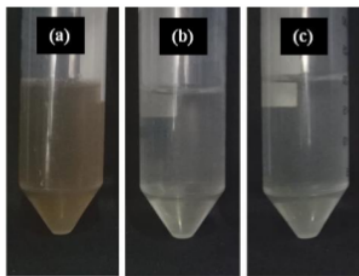

Figure 5. Comparison of samples of aqueous liquid waste (a) before adsorption; After treatment using adsorbent (b) RHB-M and (c) RHB-MH
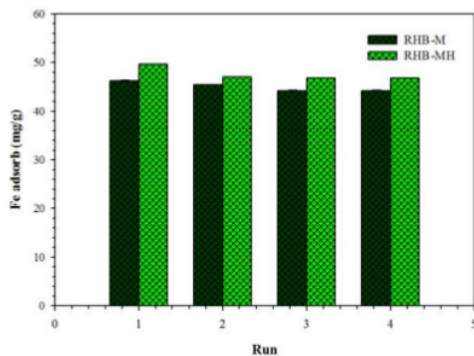
Figure 6. Reusability of the Adsorbent on the adsorption process with a sample volume of 100 mL, 0.05 g of adsorbent mass, stirring speed of 150 rpm at 60 min.

Fig 6 shown the decreased of Fe^{3+} ion adsorption capacity after 4 repeated used, the number of RHB-M ad RHB-MH about 4.48% and 5.86%, respectively. This was possible because of the reduced concentration of H^+ ions that play a significant role in the adsorption process during washing. This

shows that RHB-M and RHB-MH adsorbents have good performance and were still effective for reused as adsorbents.

4. Conclusion

The biocomposite magnetic nanoparticle was successfully prepared by solvothermal method using rice husk fibre. Optimum condition of iron adsorption at pH 5 for 60 min which gave up high takes capacity 52.46 mg/g and TSS was reduced about 87.5% for RHB-MH. The color content in aqueous solution also could be reduced about 85.81% by RHB-MH. The biocomposite magnetic nanoparticle is candidate material for adsorb metal ion and color/dye in aqueous solution.

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