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Synthesis of Magnetic Chitosan Composite Beads as an Adsorbent for Removal of Organic Matter from Peat Water

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Abstract

Groundwater in peatlands has the potential to be utilized as a water source, but its high organic matter content presents challenges. This study aimed to improve the quality of peat water through the adsorption of organic matter using chitosan magnetic beads composite adsorbent. Magnetic chitosan beads (KMB) composite was synthesized by mixing chitosan, acetic acid, and a mixture of Fe^{2+}/Fe^{3+} solution with a mole ratio of 1:2. This mixture was then dropped into a sodium hydroxide solution. In addition to KMB, magnetic composite beads containing glutaraldehyde crosslinking agent (KMBG) were also synthesized. The results of composites analysis using a Fourier transform infrared (FTIR) spectrophotometer showed typical Fe-O absorption bands at 582 cm^{-1} and 578 cm^{-1} for KMB and KMBG. The typical C=N absorption band for glutaraldehyde in KMBG appeared at 1631 cm^{-1}. X-ray diffraction (XRD) analysis revealed the characteristic peaks of Fe_3O_4 for KMB and KMBG at 2θ = 30.2°, 35.5°, 43.2°, 57.0°, and 62.8° with an amorphous structure. The adsorption of organic matter was performed by varying the pH (2, 3, 4, and 5) of peat water and the mass of the adsorbent (50, 70, 100, 200, and 300 mg). The optimum adsorption occurred at pH 2 with an absorbent mass of 0.1 g KMB and 0.07 g KMBG. Applying KMB on peat water reduces turbidity, color, and absorbance at a wavelength of 254 nm ($A_{\lambda=254}$), which is better than using KMBG. These three parameters' efficiency percentages were 44%, 78%, and 74% for KMB and 17%, 30%, and 59% for KMBG.

1. Introduction

Surface water available in peat areas (known as peat water), which is acidic and yellow to brown in color, is a possible potential source of water that can be processed into clean water and even drinking water, providing the organic matter concentration is lowered to satisfy quality standards. Several methods have been widely applied in peat water treatment to remove organic matter, such as adsorption [1], coagulation-flocculation [2], and membrane separation [3]. Adsorption is preferred because it is more economical, easy to use, highly efficient, and can remove unwanted compounds [4]. One type of adsorbent that has been widely studied is chitosan. Chitosan is biodegradable and biocompatible and has many active groups in the form of OH and NH_2. Under acidic conditions, NH_2 is protonated to NH_3^+ and can interact with heavy metals, dyes [4], and organic matter [5]. However, separating the adsorbent from the solution at the end of the adsorption process is becoming an issue because its process is time-consuming and costly. This issue can be resolved by producing a magnetic chitosan composite that enables rapid and easy separation of the adsorbent from the solution with the assistance of an external magnet.

Wang *et al.* [5] have composited magnetite into chitosan to reduce organic matter content, such as commercial humic acid at a concentration of 10 mg/L. A composite of 0.7 g/L can reduce the humic acid content by 16% within 80 minutes. Physical and chemical modifications are generally conducted to improve the quality of chitosan as an adsorbent for broader applications. The physical modification involved changing chitosan from powder to beads in order to enhance its adsorption capacity and accelerate its kinetics [6]. Meanwhile, the chemical modification was performed by adding a crosslinker compound to increase the chemical stability of chitosan in an acid solution [7].

Dong *et al.* [8] have synthesized chitosan magnetic beads added with epichlorohydrin as a crosslinker agent to increase the chemical stability of chitosan and its absorption capacity to adsorb commercial humic acid. The adsorbent mass of 0.1 g/L can reduce organic matter by 50% within 10 minutes with a pH solution of 4, reach equilibrium in 60 minutes, and have an adsorption capacity of 32.6 mg/g. Other crosslinker compounds that have been utilized in the production of chitosan magnetic bead composites include H_2SO_4 for dye removal [9] and sodium citrate for heavy metal adsorption [10]. However, several types of crosslinker compounds have carcinogenic properties and are more dangerous when compared to other crosslinker compounds, such as glutaraldehyde [11]. Rahmi *et al.* [12] have synthesized chitosan composited with magnetite from iron sand and crosslinked with glutaraldehyde to reduce mercury in wastewater. The results demonstrated that adding Fe_3O_4 and glutaraldehyde lowered the crystallinity of chitosan and decreased mercury levels in the wastewater by 96.13%. Rani *et al.* [13] also synthesized chitosan magnetic beads added with glutaraldehyde crosslinker compound for nickel removal.

Based on previous publications, it is known that magnetic chitosan beads have been used for humic acid adsorption. Magnetic chitosan beads with a crosslinker have been applied for heavy metal adsorption. The success of chitosan magnetic beads without a crosslinker in adsorbing humic acid is the basis for this research to employ this adsorbent in peat water treatment. Peat water contains humic acids and other dissolved organic and inorganic materials such as metal oxides. The chitosan magnetic beads will have glutaraldehyde added as a crosslinker to enhance performance. This study aimed to synthesize composite magnetic chitosan beads and magnetic chitosan-glutaraldehyde as adsorbents to improve peat water quality. Indicators of organic matter reduction in peat water can be observed from changes in color, pH, turbidity, and absorption measurements at a wavelength of 254 nm ($A_{\lambda=254}$).

2. Methodology

2.1. Instruments and Materials

The instruments used were FTIR spectrophotometer (Shimadzu IR-Prestige 21), a pH meter (Hanna), XRD (Philips X-Pert XMS), a UV-Visible spectrophotometer (Shimadzu UV-2600), and turbidimeter (Hach 2100Q). The chemicals used include 100% glacial acetic acid (1.04 g/cm^3) (Merck), 37% hydrochloric acid (1.18 g/cm^3) (Merck), iron (III) chloride hexahydrate (Merck), iron (II) heptahydrate sulfate (Merck), 25% glutaraldehyde (1.06 g/cm^3) (Sigma Aldrich), sodium hydroxide (Merck), commercial chitosan (DD: 85%), and peat water.

2.2. Preparation of Peat Water

Peat water was taken from waterways around the Universitas Tanjungpura area. Peat water was collected using a bucket and put into a plastic jerry can. The peat water was then filtered and characterized by measuring pH, turbidity, color, and $A_{\lambda=254}$. Peat water was stored in the refrigerator for future use.

2.3. Production of Magnetic Chitosan Composite Beads (KMB)

Magnetic chitosan composite beads were manufactured using a method that referred to previous studies [10] with several modifications. Chitosan (0.8 g) was completely dissolved in 40 mL of 2% (v/v) acetic acid solution and stirred for 1 hour. A mixed solution of Fe^{2+}/Fe^{3+} was prepared by dissolving iron (II) sulfate heptahydrate and iron (III) chloride hexahydrate with a mole ratio of $Fe^{2+}:Fe^{3+}$ of 1:2 in 10 mL of distilled water. Furthermore, 10 mL of Fe^{2+}/Fe^{3+} solution was added to the chitosan solution and stirred for 1 hour. The mixed solution was then dripped into 0.5 M sodium hydroxide solution with a syringe to form beads and left to soak for 24 hours. After soaking, the beads were washed with distilled water until the pH was neutral.

2.4. Production of Glutaraldehyde-crosslinked Magnetic Chitosan Beads (KMBG)

The addition of a crosslinker to the chitosan magnetic composite beads was conducted, referring to previous studies [13], by employing a magnetic chitosan beads composite soaked in a 0.025 M glutaraldehyde solution for 24 hours. After that, the magnetic chitosan beads were washed several times with distilled water to remove residual glutaraldehyde and then dried in an oven at 40°C for 24 hours.

2.5. Characterization of KMB and KMBG

The characterization of KMB and KMBG using FTIR and XRD spectrophotometers was performed at the Hassanudin University Microbiology Laboratory and the Metallurgical Laboratory of the Sepuluh November Institute of Technology, respectively.

2.6. Determination of The Optimum pH

The procedure for determining the optimum pH for reducing organic matter from peat water refers to the research of Kristianto *et al.* [14] with some modifications. Each KMB and KMBG (100 mg) was added into each bottle containing 100 mL of peat water, where the pH of the peat water was varied to 2, 3, 4, and 5 by adding 0.1 M hydrochloric acid solution, then stirred using a shaker at 210 rpm for 30 minutes. The mixture was allowed to stand and separated using a magnet and observed for the highest decrease in color intensity.

2.7. Determination of Optimum Mass

The procedure for determining the optimum mass for removing organic matter from peat water refers to the research of Kristianto *et al.* [14] with several modifications. Each KMB and KMBG was added into 100 mL of peat water at optimum pH with the different masses of the beads of 50, 70, 100, 200, and 300 mg, then stirred using a shaker at 210 rpm for 30 minutes. The solution was separated using a magnet, and the obtained filtrate was tested for color, turbidity, pH, and $A_{\lambda=254}$. Color and $A_{\lambda=254}$ in peat water were measured using a UV-Vis spectrophotometer at 455 nm and 254 nm, respectively. Meanwhile, turbidity and pH were determined using a turbidimeter and a pH meter. The reduction efficiency of $A_{\lambda=254}$, color, and turbidity in peat water can be calculated by equation (1).

$$(\%)\ removal = \frac{A_i - A_t}{A_i} \text{ x } 100\% \qquad (1)$$

where, A_i and A_t are initial and final absorbance, respectively.

3. Results and Discussion

3.1. Preparation of Peat Water

The peat water used in this study was obtained from waterways in the Universitas Tanjungpura area. The surface peat water was collected with a bucket and filtered to remove pollutants such as leaves and branches. After that, the parameters pH, turbidity, color, and $A_{\lambda=254}$ were measured. Furthermore, peat water was stored in the refrigerator. The results of peat water quality measurements can be seen in Table 1.

Table 1. Peat Water Quality Parameters

Parameters	Tested Sample	Regulation of Minister of Health Number 32 of 2017
pH	4.3	6-8.5
Turbidity	4.74 NTU	5 NTU
Color	850 Pt. Co	50 Pt. Co
$A_{\lambda=254}$	3.065	-

3.2. Synthesis of Adsorbents

3.2.1. Synthesis of KMB and KMBG

The coprecipitation method was employed to produce magnetic chitosan beads by first preparing a chitosan solution, adding a mixture of iron solution to the chitosan solution to form chelation, and then completing the formation of gel beads. The results of the synthesis of KMB and KMBG are shown in Figure 1.

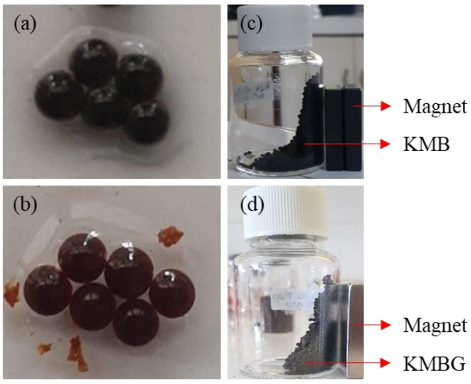

Figure 1. (a) KMB and (b) KMBG synthesized results, as well as the appearance of the magnetic properties of (c) KMB and (d) KMBG

Figure 1 (a) demonstrates that KMB generates black beads, indicating that the beads contain magnetite material, whereas Figure 1 (b) shows that beads are blackish brown which shows that some of the beads are undergoing oxidation during the immersion process in glutaraldehyde solution [15]. In addition, the existence of magnetite in the composite is depicted in Figures 1 (c and d), indicating that KMB and KMBG have good magnetic properties, as supported by the attraction of the sample following the direction of the magnetic field. The synthesized KMB and KMBG were then characterized using FTIR and XRD.

3.2.2. Characterization of KMB and KMBG

FTIR analysis was employed to identify the characteristic functional groups of the synthesized KMB and KMBG. Measurements were made in the wavelength range of 4000–500 cm⁻¹. The results of measurements using the FTIR spectrometer on the KMB and KMBG can be seen in Figure 2.

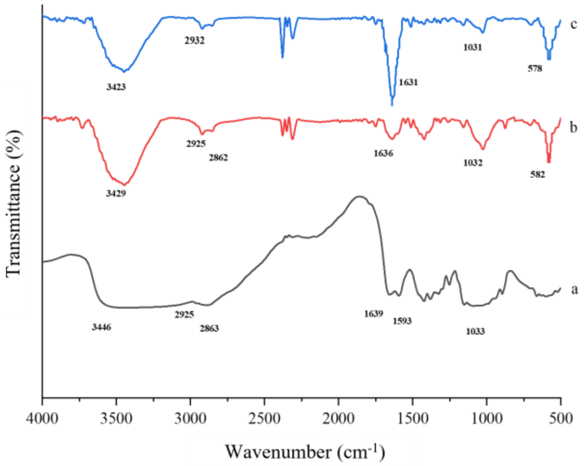

Figure 2. FTIR spectra of (a) chitosan, (b) KMB, (c) KMBG

Figure 2 (a) depicts the spectrum of pure chitosan as shown by the emergence of a peak at 3446 cm⁻¹, indicating O–H stretching vibrations that overlap with N–H vibrations. The band at 2863 cm⁻¹ is characteristic of C-H stretching vibration. The wavenumber of the 1639 cm⁻¹ region indicates the absorption of amide bonds in chitosan [12]. Figures 2 (b and c) show the appearance of new peaks at 582 cm⁻¹ and 578 cm⁻¹, which correspond to vibrations of the Fe-O bond typical of Fe_3O_4 [12]. The addition of glutaraldehyde results in the appearance of absorption at 1631 cm⁻¹, indicating a C=N bond vibration in the form of a Schiff base [16], which overlaps with the bond vibration at 1639 cm⁻¹ [17]. In addition, the shift in wavenumber from 2925 cm⁻¹ to 2930 cm⁻¹ indicates an increase in the amount of CH_2 in the composite structure due to its reaction with glutaraldehyde. Similar results were also found in previous studies [15, 18]. Based on Figure 2, the KMB and KMBG composites were successfully synthesized.

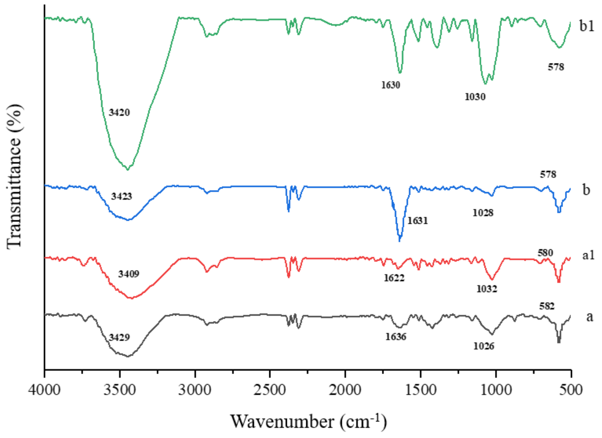

Figure 3. FTIR spectrum of KMB (a) before adsorption and (a1) after adsorption, KMBG (b) before adsorption and (b1) after adsorption

KMB and KMBG were also characterized after being applied as adsorbents to reduce organic matter in peat water. The results of the FTIR measurements are shown in Figure 3. In the spectrum of a1 and b1, there was a shift in the wavenumbers from 3429 cm^{-1} to 3409 cm^{-1} and 3423 cm^{-1} to 3420 cm^{-1}. This indicates that the N atom of the amine group in chitosan plays a role in reducing organic matter in peat water by interacting electrostatically with anion groups in peat water during the adsorption process [19]. In addition, in the absorption area of 1629 cm^{-1}, there was also a shift in wave number to 1622 cm^{-1}, which was possible because the N atoms of the amide group in chitosan also interacted electrostatically with anion groups in peat water during the adsorption process [20, 21]. An overview of the proposed interactions that occur during the adsorption process is shown in Figures 4 and 5 [8, 21, 22, 23, 24].

The minerals in the synthesized composites, such as Fe_3O_4 or magnetite, are measured using XRD. The diffractograms of the KMB and KMBG are shown in Figure 6. XRD measurements on KMB and KMBG showed the presence of a peak at $2\theta = 20°$, which is a typical peak for chitosan [12]. Five characteristic Fe_3O_4 peaks, located at 2θ values of 30.2°, 35.5°, 43.2°, 57.0°, and 62.8°, were seen in the XRD patterns of KMB and KMBG after being treated with Fe_3O_4. The measurement results were compared with Hosseini *et al.* [25] in Figure 6 (b). The measurement results showed the presence of Fe_3O_4 particles in the KMB and KMBG.

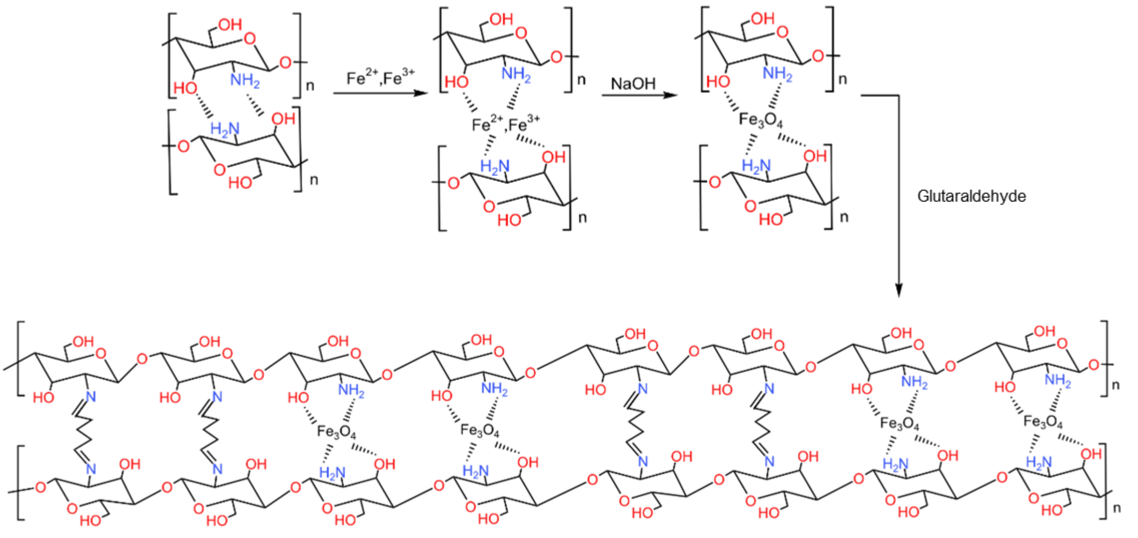

Figure 4. Reactions that may occur in the synthesis of KMB and KMBG

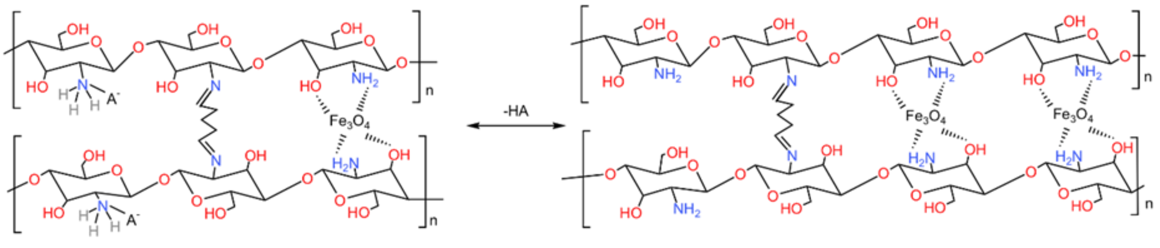

Figure 5. Reactions that may occur in the adsorption process of organic matter from peat water using KMB and KMBG

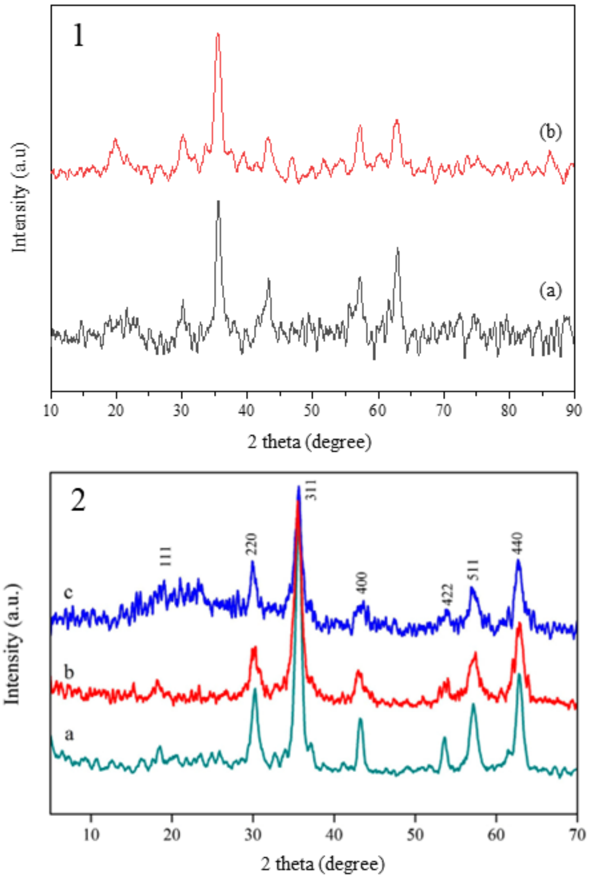

Figure 6. The pattern of diffractogram of (1) chitosan magnetic beads synthesized: (a) KMB and (b) KMBG, and (2) chitosan magnetic beads: (a) Fe_3O_4-chitosan, (b) Fe_3O_4-chitosan-TPP, (c) Fe_3O_4-chitosan-Glu [25]

3.3. Determination of Optimum Conditions for Organic Matter Removal in Peat Water

3.3.1. Determination of Optimum pH Conditions

Optimum adsorption conditions were investigated to determine the ability of KMB and KMBG in water treatment significantly to reduce organic matter in peat water. The degree of acidity or pH is an essential parameter in the water treatment process because it affects the activity of functional groups on adsorbents and organic matter during the adsorption process, where the adsorption process of organic matter will increase with decreasing pH of the solution [26]. The pH variations used in the experiment were 2, 3, 4, and 5, with an adsorbent mass of 100 mg in 100 mL of peat water and a stirring speed of 210 rpm for 30 minutes. The results of the optimum pH determination experiment are shown in Figure 7.

Figure 7. The effects of pH variations on changes in the color of peat water are as follows (left to right): peat water before adsorption, adsorption at pH 5, 4, 3, and 2

Figure 7 demonstrates that pH 2 exhibits the highest color reduction results compared to other pHs. According to Lerebulan *et al.* [27], the more concentrated the color of the solution, the higher the concentration of organic matter; conversely, the more faded the color of the solution, the lower the concentration of organic matter. Based on the zeta potential value, it states that at a pH solution above 1.5, the organic matter contained in peat water will be negatively charged due to the dissociation of H^+ ions from carboxyl. Chitosan will be positively charged at a solution pH below 7 due to protonation of the functional group in the form of NH_2 to NH_3^+. Negatively charged organic matter will interact with the positively charged adsorbent surface so that adsorption interactions at low pH conditions are electrostatic interactions between protonated amine groups in chitosan (NH_3^+) and carboxyl groups of dissociated organic matter (COO-). The organic matter is reduced more effectively at pH 2 than at pH 3 since the amine group of chitosan undergoes complete protonation, improving its ability to interact with negatively charged organic materials at low solution pHs [8]. These results are in accordance with previous research, which showed that decreasing color due to reduced organic matter increased with decreasing pH of the solution and vice versa, decreasing color due to organic matter decreased with increasing pH of the solution [28].

3.3.2. Determination of Optimum Mass

The process of determining the optimum mass was done to assess the impact of more beads on the peat water treatment process. The different bead masses utilized vary from 50, 70, 100, 200, and 300 mg in 100 ml of peat water with a pH of 2 and an agitation speed of 210 rpm for 30 minutes. The results of determining the optimum mass of KMB and KMBG adsorbents in peat water are shown in Figure 8.

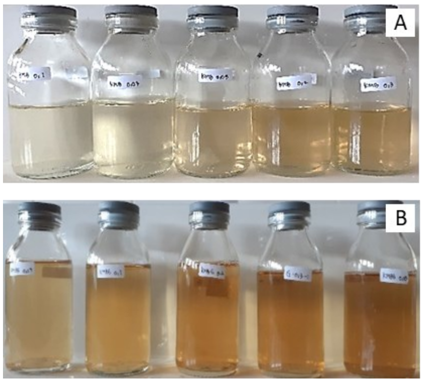

Figure 8. Results of determining the optimum mass of (A) KMB from left to right (0.1, 0.07, 0.05, 0.2, and 0.3 g) and (B) KMBG in decreasing peat water organic matter from left to right (0.07, 0.1, 0.2, 0.3, and 0.05 g)

Based on physical observations from Figure 8, it can be seen that the highest color decrease occurred in the adsorption process using beads with 0.1 g for KMB and 0.07 g for KMBG. Water quality measurements were made using the parameters of turbidity, color, pH, and $A_{\lambda=254}$ to determine the quality of the peat water before and after adsorption with the KMB and KMBG adsorbents. Based on Figure 9, it can be seen that KMB is much better at reducing turbidity than KMBG. The result was that the more beads added, the higher the efficiency of reducing turbidity; however, after adding 0.1 g of mass to KMB, the turbidity increased. This happened because the adsorbent was damaged due to the decreased stability of chitosan at low pH.

The glutaraldehyde crosslink was added to the KMBG composite to increase chitosan's stability. However, the results obtained with the KMBG adsorbent revealed a lower reduction efficiency than the KMB adsorbent. The turbidity was further increased by adding mass after 0.07 g. The turbidity reduction efficiency using KMB and KMBG adsorbents was 44% and 17%, respectively.

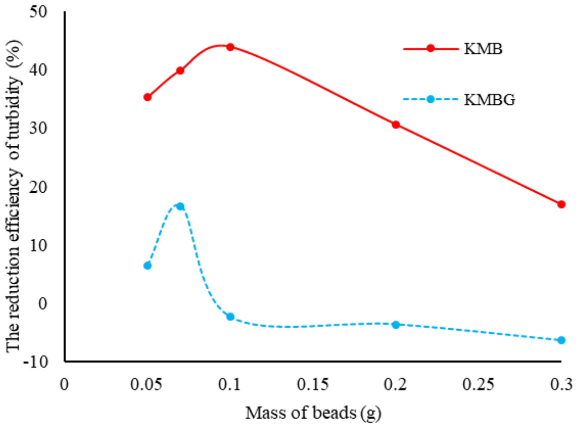

Figure 9. Graph of the effect of the mass of the beads on the decrease in turbidity

The same results were also obtained for measuring the color parameters and $A_{\lambda=254}$, as shown in Figure 10 and Figure 11. Based on these figures, it can be seen that the KMB adsorbent has a higher efficiency of color reduction and absorbance compared to the KMBG adsorbent, which is 78% for color and 74% for $A_{\lambda=254}$, while the reduction efficiency using KMBG adsorbent is 30% for color and 59% for $A_{\lambda=254}$. The optimum masses for each KMB and KMBG adsorbent occurred at 0.1 g and 0.07 g.

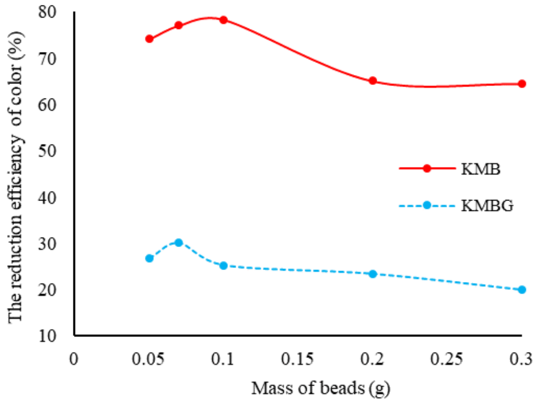

Figure 10. Graph of the effect of the mass of the beads on the decrease in color

The KMB adsorbent performed better than the KMBG adsorbent in terms of efficiency in reducing turbidity, color, and $A_{\lambda=254}$ due to the abundance of the active group NH_3^+ on the adsorbent KMB. The reduction of the active groups in the KMBG adsorbent occurred due to a glutaraldehyde crosslink. The active group on the adsorbent diminishes as a result of binding to the Fe group from magnetite and the aldehyde group from glutaraldehyde due to the interaction between the aldehyde group of glutaraldehyde and the NH_3^+ group of chitosan [21]. This causes the efficiency of the KMBG adsorbent to decrease during the adsorption process, as shown in Figures 4 and 5.

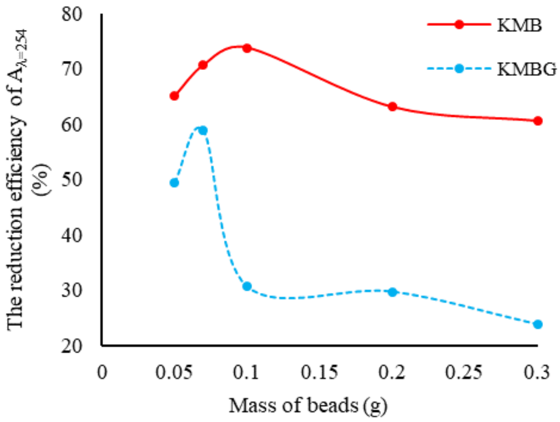

Figure 11. Graph of the effect of the mass of the beads on the decrease in $A_{\lambda=254}$

The results of pH measurements after the adsorption process are shown in Figure 12. As can be observed, the mass of the adsorbent directly correlates with the rise in the pH of the peat water, with the pH of the peat water increasing as more mass of the beads is utilized. The pH of the solution rises as the mass of the beads increases, indicating a decrease in the amount of organic matter in the peat water. The best results were found at 0.3 g for KMB and KMBG. However, these results fall short of the clean water quality requirements outlined in the Regulation of the Minister of Health of the Republic of Indonesia No. 32 of 2017, which states that water is suitable for use if its pH is between 6.5 and 8.5. Therefore, additional processing is required to raise the pH of peat water to satisfy current quality standards.

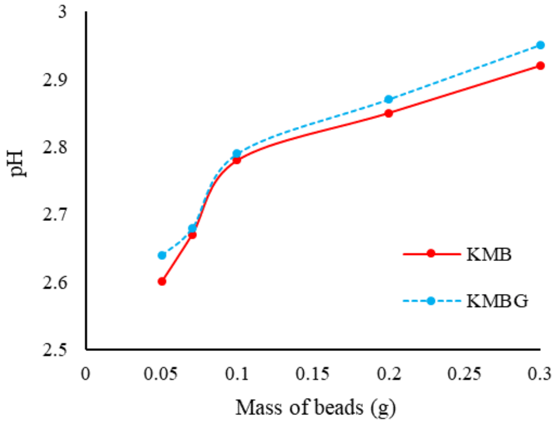

Figure 12. The graph of the relationship between the mass of the beads and the pH solution

4. Conclusion

Based on the research that has been done, it can be concluded that the presence of magnetite in KMB and KMBG was indicated by typical Fe-O absorption at 582 cm⁻¹ and 578 cm⁻¹. The presence of glutaraldehyde in

KMBG was found at 1631 cm^{-1}. XRD results showed a typical peak of Fe_3O_4 at 2θ value 30.2°, 35.5°, 43.2°, 57.0°, and 62.8°. The efficiency of reducing turbidity, color, $A_{\lambda=254}$ using the KMB adsorbent was better than the KMBG adsorbent, with the efficiency percentages of the three parameters being 44%, 78%, 74% for KMB and 17%, 30%, and 59% for KMBG. Additionally, it is known that KMB can be used to decrease organic matter in peat water; however, additional processing is required to raise the pH of peat water following the adsorption process in order to fulfill current quality standards.

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