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Application of the Composite Hydrotalcite (Mg/Al)/Chitosan as Adsorbent for the Treatment of Raw Water of Municipal Waterworks PDAM Bandarmasih

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ABSTRACT

This research has been carried out about raw water treatment of Municipal Waterworks PDAM Bandarmasih using composite of hydrotalcite (Mg/Al) and chitosan (from of Haruan and Papuyu fish) by adsorption process of color (PtCo), iron (Fe), and turbidity values. This research intended to produce raw drinking water from the utilization of the composite hydrotalcite (Mg/Al)/chitosan as adsorbent with variations doses of 1, 2 and 3 g/L within 24 hours, stirrer rate of 200 rpm at room temperature. The results showed that the decrease in color value was 96.78%, 95.03%, and 92.98%. Percentage decrease in iron (Fe) was 94.38%, 93.78 and 91.87% and percentage of turbidity reduction were 97.98%, 79.76%, and 76.56%. Optimum condition in variations of hydrotalcite (Mg/Al)/chitosan dose was 1 g/L for a duration of 24 hours, 200 rpm at room temperature, where at that condition resulted in a decrease in color, iron and turbidity become of 11 PtCo, 0.47 mg/L, 0.76 NTU. The results were appropriate in the drinking water requirements in accordance with the Regulation of the Minister of Health of the Republic of Indonesia No: 492/MENKES/PES/IV/2010.

Keywords: hydrotalcite (Mg/Al), chitosan, color, iron, turbidity, raw water

INTRODUCTION

The human population in South Kalimantan according to Badan Pusat Statistik in 2016 is around 4 million, while for Banjarbaru the community is almost 250 thousand, resulting in a problem, one of which is liquid waste. Adsorption is one effective way to eliminate a component that is not desired. Many researchers had been researched adsorption mainly with hydrotalcite because it has a large surface area and it has a synergistic effect between layers so that it attracts the interest of researchers.

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Heraldy et al. research (2012) found that the utilization of PLTU distillation waste for the manufacture of Mg/Al hydrotalcite of methyl orange (MO) adsorption resulted in a MO adsorption rate of 7.30×10^{-4} seconds. Imaniah (2016) has researched the comparison of $Mg/Al\text{-}NO_3$ hydrotalcite-magnetic composites (HT-M) and $Mg/Al\text{-}NO_3$ hydrotalcite-magnetic calcination as adsorbent to eliminate remazol yellow dye, where the result was HT-M optimum adsorbed dyes as much as 7.67×10^{-5} mol/gram at pH 4 with a reaction time of 90 minutes and HT-MKAL of dyestuffs which optimum adsorption was 7.74×10^{-5} mol/gram at pH 3 within 90 minutes.

The hydrotalcite (Mg/Al)+chitosan study which is chitosan obtained from local fish scales in the Banjarmasin wetland area. The chitosan is used as an adsorbent to deal with the PDAM Bandarmasih raw water problem in

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Banjarmasin. Its found that the parameters are not following drinking water according to the regulation standards of the Minister of Health of the Republic of Indonesia No 492/MENKES/PER/IV/2010. Resulted from the analysis of the PDAM office state that color (Pt-Co) 342, turbidity of 37.55 (NTU), and iron (Fe) concentration in the raw water of 0.836 mg/L, while the requirements for drinking water are 15 PtCo, 5 NTU, and 0.3 mg/L, respectively. Therefore the parameters needed to be treated.

MATERIALS AND METHODS

Materials and Methods

Chitosan derived from original fish scales of Kalimantan called Haruan (*Channa striata*) and Papuyu (*Anabas testudineus*). The other materials used in this research are 40% NaOH, HCl (0.275–1 N), $Al(NO_3)_3.9H_2O$ 0.01 N, $Mg(NO_3)_2.6H_2O$ 0.05 N, $NaCO_3$ 0.1 M, distilled water, acetic acid glacial (Merck) 2% (b/v), $NaHCO_3$ 0.05 M, NaOH 0.1 M, NaOH (0.25–2.5N), concentrated HCl (Merck), chitosan, raw water of Municipal Waterworks PDAM Banjarmasin.

Chitosan will be extracted by (No and Meyers, 1995) method with some modifications. Chitosan synthesis involves three significant steps such as deproteinization (using NaOH), demineralization (using HCl) and deacetylation processes.

Chitosan Preparation from Fish Scales

Deproteinization

A solution of NaOH with a concentration of 3.5% is mixed with fish scales and heated at a temperature of 65°C. When heated, the mixture is stirred using a magnetic stirrer for 2 hours. The mixture is cooled at room temperature (25°C), then filtered while washing using distilled water. The mixture is heated for 24 hours at 65°C.

Demineralization

HCl 1N solution is mixed with the fish scale of deproteinized, then heated for 1 hour at 65°C. The mixture is stirred using a magnetic stirrer and cooled at room temperature. The mixture is filtered while rinsed using distilled water, then dried into the oven for 24 hours at 65°C.

Deacetylation

Chitin which was obtained in the previous stage is immersed in a 50% NaOH solution while heated at 100 ° C for 4 hours. The mixture is stirred using a magnetic stirrer and then cooled to room temperature. After that washed using distilled water and immediately oven for 24 hours at 65 °C and the results obtained were weighed using an analytical balance, producing chitosan around 75% yield.

Preparation of Composite of Hydrotalcite (Mg/Al) into Chitosan by Co-Precipitation Process

Mg-Al (NO_3) with a ratio of 2 molar Mg^{2+}/Al^{3+} is synthesized using the coprecipitation method. 70 mL solution containing 0.01 mol of $Mg(NO_3)_2.6H_2O$ and 0.05 mol of $Al(NO_3)_3$. $9H_2O$ is added drop by drop into 0.1M NaOH and 2M Na_2CO_3 solution until a solution of 1000 mL is obtained. The mixture is heated at 45°C with a mixing speed of 200 rpm.

One gram of chitosan is added to the mixture which is then dissolved in acetic acid by 2% (b/v), and dissolved in hydrotalcite (Mg/Al) while heating for 2 hours at 85°C. The mixture is decanted for 12 hours and separated the top solution and bottom solution by pipette using a volume pipette. Then washed using distilled water until clean and dried using an oven at 60°C for 24 hours, later it is grounded into powder.

Treatment Process of Raw Water PDAM Bandarmasih using Composite Mineral Hydrotalcite (Mg/Al) and Chitosan as Adsorbent

Three beaker glass with a size of 1000 mL filled with raw water from PDAM Bandarmasih, then adding hydrotalcite chitosan for 1, 2 and 3 grams for each beaker glass. The mixture is then stirred at a speed of 200 rpm for 1 hour. The recycle usage of such adsorbent was repeated for three times in triplicate analysis.

RESULTS AND DISCUSSION

Indonesia is famous for its maritime country because the sea area is more than the plain, so it is rich in marine products, especially fish, for example in Banjarmasin which is famous for 1000 rivers and wetlands where wetlands are used to cultivate fish primarily local fish (Haruan and Papuyu). The need for fish is increasing every year which results in problems especially fish scales which are disposed of uselessly.

Fish scales are still not widely used in Indonesia where only 20% is used to mixed animal feed ingredients and the rest even cause problems. This study aims to reduce the problem where these untapped fish scales can be used as chitosan which has many benefits, for example as natural preservatives, environmentally friendly bioplastics, natural ingredients in combination with other compounds and wastewater treatment where the results of this research are obtained chitosan from scales of Haruan and Papuyu fish.

Chitosan obtained from the deacetylation process can be measured DD% from the results using FTIR analysis as shown in Figure 1.

The FTIR results can be calculate DD% by the formula proposed by (Domszy and Roberts, 1985) based on the Baxter Method.

A_{1649}= log (%T), A_{3462}= log(%T)

$DD\% = 100-(A_{1649}/A_{3462} \times 100/1.33)$

where:

DD : degree of deacetylation.

A_{1649} : adsorbent at wave number 1649 cm^{-1} which shows carbonyl uptake of amide.

A_{3462} : adsorbent at wave number 3462 cm^{-1} which is hydroxyl absorption.

DD is one of the chemical characteristics of DD% calculation to find out this is chitosan or still chitin if DD is 75% or more, it can be said to be chitosan (Azhar et al. 2010). The DD% obtained from the above calculation is 77.94% where chitosan obtained is combined again with hydrotalcite to increase the pores and extend the adsorbent surface so that the absorbency is faster. This can be proven by the SEM results obtained between chitosan and hydrotalcite(Mg/Al)/ chitosan (Figure 2).

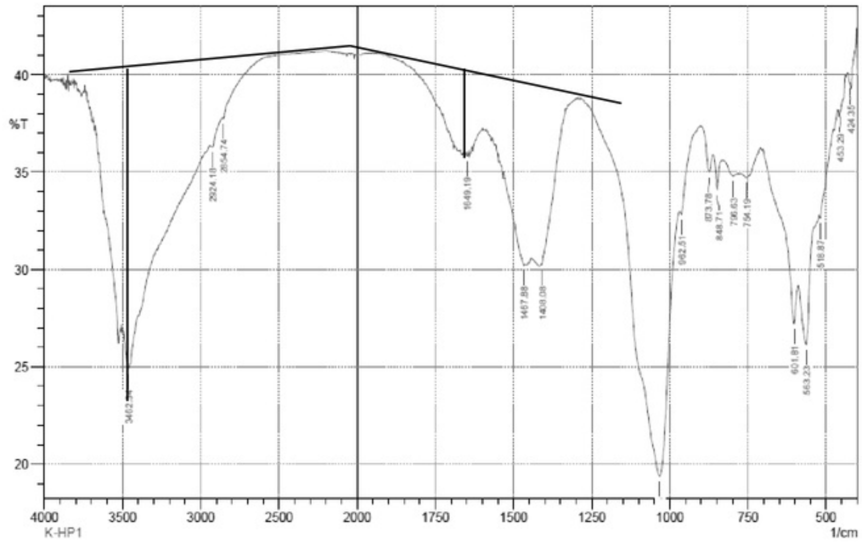

Figure 1. FTIR analysis of chitosan from Haruan and Papuyu fish scales

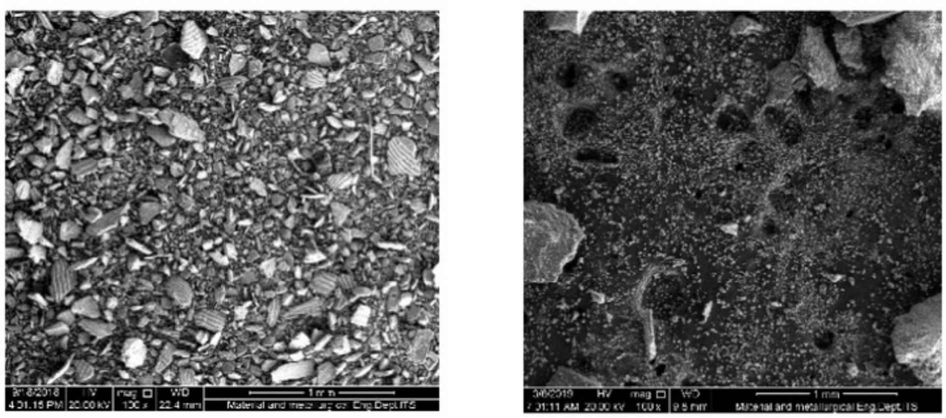

Figure 2. SEM morphology of (a) Chitosan (b) Hydrotalcite (Mg/Al)/Chitosan

The SEM results in figure 2 shown that the composite of hydrotalcite/chitosan pores are more than the chitosan pores itself and also the hydrotalcite+chitosan is smoother on the surface, so hydrotalcite+chitosan is better in the absorption process than chitosan.

Raw sources water samples taken from Bilu river, South Kalimantan at the dry season (April–June 2018). It is immediately placed in the storage cooler (below 4ºC) before use for the experiment.

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Preliminary data is obtained from the PDAM Banjarmasih itself where from the preliminary results Parameters that are not in accordance with drinking water according to the standards of regulation of the Minister of Health of the Republic of Indonesia No 492/MENKES/PER/IV/2010 and the results of analysis is found that color (Pt-Co) of 342, turbidity (NTU) of 37.55, and iron (Fe) 0.836 mg/L, while the requirements for drinking water are 15 PtCo, 5 NTU, and 0.3 mg/L, respectively. Therefore the parameters used are color, turbidity, and iron because it is not under drinking water requirements while according to the analysis data, another PDAM Bandarmasih is done accordingly. The handling of PDAM raw water is carried out by the adsorption method with hydrotalcite (Mg/Al)/chitosan composite minerals which are varied by 1, 2 and 3 grams/liter with a reaction time of 24 hours.

Table 1 shows changes the pH of the solution after and before the reaction with hydrotalcite (Mg/Al)/chitosan for 24 hours. The increase in pH after reacted with hydrotalcite adsorbent (Mg/Al)/chitosan is likely due to hydrotalcite and chitosan itself in an alkaline atmosphere this was evidenced by research by Imaniah (2016). The hydrotalcite pH is around 9-13 alkaline so it causes pH to rise according to the increase in the amount of hydrotalcite (Mg/Al)/chitosan 1, 2 and 3 grams/liter with an increase in pH of 9.29, 9.88 and 10.21. It is still safe to drink often called alkaline water with a pH range of 8-11. Where the benefits of alkaline water if consumed continuously can hamper cancer growth (Catur, 2016).

The occurrence of a decrease in color after reacted with hydrotalcite adsorbent (Mg/Al)/chitosan where the color undergoes negatively charged species dominate dissociation (Table 2). The color which causes more natural negatively charged species of dyes to interact with the surface of the hydrotalcite (Mg/Al) adsorbent and positively charged of chitosan. However, along with the increase in pH value, the higher the amount of the dye absorbed by hydrotalcite (Mg/Al)/chitosan dose decreases because the effect of high pH is assumed to be positively hydrotalcite (Mg/Al)/chitosan where the real properties diminish. pH (Heraldy, 2017) Adsorption can be influenced by several parameters, namely pH, reaction time, adsorbent dose and temperature (Zubair, 2017).

Table 1. Changes the pH of the solution after and before the reaction with hydrotalcite (Mg/Al)/chitosan for 24 hours

Hydrotalcite (Mg/Al)/chitosan (gram)	pH before reaction	pH after reaction	pH percentage change(%)
1 gram	7.49	8.29	11.00%
2 gram	7.49	8.88	19.00%
3 gram	7.49	9.21	23.00%

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Table 2. Changes in solution color after and before reacting with hydrotalcite (Mg/Al)/chitosan for 24 hours

Hydrotalcite (Mg/Al)/Chitosan (gram)	Color before reaction (PtCo)	Color after reaction (PtCo)	Percentage removal (%)
1 gram	342	11	96.78%
2 gram	342	17	95.03%
3 gram	342	24	92.98%

Table 3 shows changes in turbidity of the solution after and before reacting with hydrotalcite (Mg/Al) + chitosan for 24 hours. The occurrence of turbidity reduction after reacted with hydrotalcite adsorbent (Mg/Al)/chitosan where turbidity is also called turbidity where turbidity is caused by suspense material such as particles of colloidal organic particles where hydrotalcite (Mg/Al)/chitosan has excellent ability to separate particles of colloids with fine size can reduce the turbidity value (Imaniah, 2016).

Table 4 shows changes in iron (Fe) solution after and before reacting with hydrotalcite (Mg/Al)/chitosan for 24 hours. The decrease in iron (Fe) after reacted with hydrotalcite adsorbent (Mg/Al)/chitosan where there is a decrease in iron in the solution due to hydrotalcite (Mg/Al)/chitosan which is positively charged as a result of the persistent substitution of cations divalent by trivalent cations and has an empty interlayer area that is used to adsorb metal anions in this case iron in the solution that causes iron to dissolve after the reaction becomes a decrease where on the surface of hydrotalcite (Mg/Al)/chitosan has an electrostatic force or attractive force between metal in solution.

Table 3. Changes in turbidity of the solution after and before reacting with hydrotalcite (Mg/Al)/chitosan for 24 hours

Hydrotalcite (Mg/Al)+ chitosan (gram)	Turbidity before reaction (NTU)	Turbidity after reaction (NTU)	Percentage removal (%)
1 gram	37.55	0.76	97.98%
2 gram	37.55	7.6	79.76%
3 gram	37.55	8.8	76.56%

Table 4. Changes in iron (Fe) solution after and before reacting with hydrotalcite (Mg/Al)/chitosan for 24 hours

Hydrotalcite (Mg/Al)/chitosan (gram)	Iron before reaction(mg/L)	Iron after reaction(mg/L)	Percentage removal (%)
1 gram	0.836	0.047	94.38%
2 gram	0.836	0.052	93.78%
3 gram	0.836	0.068	91.87%

CONCLUSIONS

The composite of hdrotalcite (Mg/Al)/chitosan were successfully synthesized using co-precipitation process. Batch experimental experiment for treating raw water of municipal waterwork PDAM Bandarmasih using the composite adsorbent reduce significantly color, turbidity and iron metal in the solution. The decreasing in color due to the amount of hydrotalcite (Mg/Al)/chitosan because color are dominated by species that are negatively charged so that it is easy to interact with the surface of the adsorbent which is positively charged and therefore occurs a tensile force which causes the dye in the solution to decrease.

Turbidity is dissolved because of the ability of hydrotalcite (Mg/Al)+chitosan itself which is suitable for separating colloidal particle with fine sizing size so that it can reduce turbidity value that we know turbidity is caused by suspense material such as particle organic and particles colloid. The removal of iron (Fe) in the solution due to hydrotalcite (Mg/Al)/chitosan which is positively charged as a result of the persistent substitution of cations divalent by trivalent cations and has an empty interlayer area which is used to adsorb metal anions in this case iron in the solution it causes iron to be dissolved after the reaction becomes a decrease where on the surface of hydrotalcite (Mg/Al)/chitosan has an electrostatic force or attractive force between metals in the solution which results in a reduction.

The optimum dose of adsorbent hydrotalcite (Mg/Al)/chitosan to treating the raw water of PDAM Bandarmasih is around 1 g/L where the higher the pH the less favorable the result according to the Regulations Minister of Health of the Republic of Indonesia no: 492/MENKES/PES/IV/2010.

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