The treatment of Raw Water Sources of Drinking Water using Chitosan/Mg/Al–LDH Composites: Problem cases in Municipal Waterworks in Banjarmasin

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The treatment of Raw Water Sources of Drinking Water using Chitosan/Mg/Al–LDH Composites: Problem cases in Municipal Waterworks in Banjarmasin

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Abstract. A study was done on treatment of raw water sources for drinking water using chitosan/Mg-Al LDH (CS/Mg/Al–LDH) composites by adsorption process. An analysis on the adsorbent characterizations of FTIR, SEM and XRF showed that the CS/Mg/Al–LDH had many different functional groups and a high specific surface area for adsorption processes. The CS/Mg/Al–LDH showed high adsorption uptake capacity and selectivity for iron (Fe), turbidity, and colour in the raw water sources for drinking water in Municipal Waterworks in Banjarmasin. Therefore, the CS/Mg/Al–LDH composites have the potential to be used as an adsorbent in water and wastewater treatment.

1. Introduction

In developing countries, the problems of surface water sources contaminants such as heavy metal contents, turbidity and colour increase continuously as population increase and industrial development take place. Contaminated surface water will have potential adverse impacts affecting humans and other living things when supplied to Municipal Waterworks as raw water sources for drinking water and human daily activities. Therefore, raw water to be supplied should first be treated to ensure that it is safe to consume as drinking water, and free from harmful materials and microorganisms. This has received an increasing priority approach in the effort to mitigate water-related human health problems and diseases, reducing chemical and treatment cost [1, 2]. In this case, Martapura river in South Kalimantan, as the raw sources water of its Municipal Waterworks (PDAM Bandarmasih), still contains a high amount of iron (ca. of 2±0.5), turbidity (ca. of 40±5 NTU) and colour (350±50 Pt-Co) in rainy seasons.

The high heavy metal contents and turbidity are coupled with increased industrial and human activities [1], which cause the problem of colour in raw water sources generated from textile companies, food companies, distilleries, printing houses, etc. [3].

Treatment of contaminated raw water could be done by several methods, such as adsorption, reverse osmosis, disinfection, chemical precipitation, membrane filtration, microbial remediation, electrochemical, advanced oxidation process, sedimentation, ion exchange, and coagulation–flocculation processes [1, 4, 5]. Although many treatment processes have been utilized to treat contaminated raw water, there remains the possibility to find a more cost-effective and efficient treatment approach that reduces contamination in raw water, while avoiding adverse effect on the

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treated system using natural adsorbent such as naturally-occurring soil and mineral deposits, agricultural waste, biomass waste, and other accessible waste materials [1, 6, 7].

Currently, some researchers have developed organic-inorganic composites with the presence of biopolymers and minerals, which are low cost, have a high biocompatibility, biodegradability, absence of toxicity and highly efficient. This, however, attracted consideration attention to their thermal stability, functional properties and structure [8]. The methods employed for the synthesis of organic polymers–LDH composites were chemical co-precipitation, ion-exchange, and reformation of calcined LDH in the existence of organic polymers [8, 9]. The CS-LDH composites with abundant functional groups contained hydroxyl, acetyl and amino groups which have a high removal uptake capacity and rapid adsorption process for cation in aqueous solution [10].

This research aims to experimentally consider the synthesis of novel chitosan-Mg/Al–LDH composites, where the chitosan would be made from local fish scales [11] and then be applied for the treatment of contaminated raw water sources by using chitosan-Mg/Al–LDH composites as adsorbent. This research also aims to determine the effectiveness of CS/Mg/Al–LDH composites for the efficiency and uptake density of turbidity and colour removal, to determine the optimal conditions for the adsorption process, and then to compare the results with those of adsorption process using chitosan and Mg/Al–LDH as an adsorbent for the contaminated raw water treatment.

2. Materials and Methods

Samples of raw water sources for drinking water were taken from Martapura river in South Kalimantan during the rainy season (November 2018–March 2019). Iron (Fe) was measured by ICP-OES instrument, turbidity parameter (in NTU) was checked using U-50 Horiba series Multi-parameter water quality checker, while color (in Pt-Co) by UV-Vis photometer. Chitosan was well prepared from fish scales, 1 wt % in 1% acetic acid at room temperature with deacetylation degree of 90–96% [11]. The $Al(NO_3)_3.9H_2O$, $Mg(NO_3)_2.6H_2O$, glacial acetic acid and other chemicals were in pure grade analytical forms obtained from Aldrich and used without further purification.

2.1. Synthesis of chitosan/Mg/Al–LDH composites

The chitosan-hydrotalcite (CS/Mg/Al–LDH) composite was made using a simple chemical co-precipitation method. It started by dissolving aluminium nitrate, $Al(NO_3)_3.9H_2O$ (0.01 mol) and magnesium nitrate, $Mg(NO_3)_2.6H_2O$ (0.05 mol) in deionized water (70 mL) and kept as "A" solution. Then a 100 mL solution consisting of natrium carbonate, Na_2CO_3 (0.1 mol) and natrium hydroxide, NaOH (0.35 mol) was adjusted and called "B" solution. The "A" solution was then slowly mixed into the "B" solution. Next, 1 g of chitosan was dissolved in a 2% (m/v) glacial acid solution which was added to the above mixture at a steady-state stirring of 150 rpm for 3 hours to obtain a homogeneous solution. The resulting mixtures was then maintained at 110 ° C for 24 hours in a Teflon coated stainless steel autoclave. Afterwards, the resulted solid product was separated by centrifugation, washed with warm water until the pH of the solution was neutral and dried under vacuum for 24 hours. Finally, the dried CS/Mg/Al–LDH was mashed into uniform powder [12]. The structure morphology properties and chemical composition properties of chitosan, Mg/Al–LDH, and CS/Mg/Al–LDH were characterized using Fourier Transform Infra-Red (FTIR), scanning electron microscopy (SEM) and X-ray fluorescence (XRF). The surface morphology of the composite, chitosan and Mg/Al–LDH were observed by Scanning electron microscopy (SEM, JOEL JSM-6500F) with energy-dispersive X-ray spectroscopy (EDAX), and Elemental Analysis by Energy Dispersive X-ray Fluorescence (PANalytical's MiniPal 4 energy-dispersive EDXRF bench-top spectrometer) to conclude the identity and quantities of elements in the samples.

2.2. Batch Adsorption Experimental of Contaminated Raw Water

Batch adsorption experiments were carried out by putting 100 mL of raw water in 250-mL plastic bottles and adjusting its pH values with NaOH, 2M and nitric acid, HNO_3, 2M. A weighted amount of the adsorbent (CS/Mg/Al–LDH) was then added into plastic bottles. The mixture of sample solution

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and adsorbent was placed in a magnetic stirrer at 150 rpm for a certain time at room temperature. At the end of the adsorption process, the solution was centrifuged and filtered by using a 0.2 μm PVDF membrane. Finally, the filtrates were analyzed for residual turbidity and color concentration. Turbidity was measured by Hach 2100Q Portable Turbidimeters and the color was analysed using PFX-995/P Colorimeter testing Pt-Co Color, DC Scientific. Adsorbed turbidity and color were calculated from the difference between the initial and equilibrium concentrations. The adsorption process experiments were done on triplicate samples and the average value was taken. The result of composite adsorbent was then compared to the chitosan and Mg/Al-LDH itself as adsorbents. The data from experiment were fitted and pattern figured out by Sigma Plot® version 10 of software.

3. Results and Discussion

3.1. Characterizations of chitosan/ Mg/Al–LDH Composite

An FTIR analysis was employed to determine the chemical composition of chitosan/Mg/Al–LDH composite as adsorbent. This analysis would ensure the formation of chitosan and also the degree of deacetylation of the material.

Peak (λ)	Vibration type
3462.34	OH stretching, NH(-NH_2) stretching
2924.18	CH(-CH_2-) stretching asym
2854.74	CH(-CH_2-) stretching sym
1649.19	C=O(-$NHCOCH_3$-) stretching (weak)
1467.88	NH(R-NH_2) bending
1408.08	CH(-CH2-) bending asym
1382.08	NO_3^- bending
1031.95	CN stretching, C-O(-O-C-O-) stretching sym

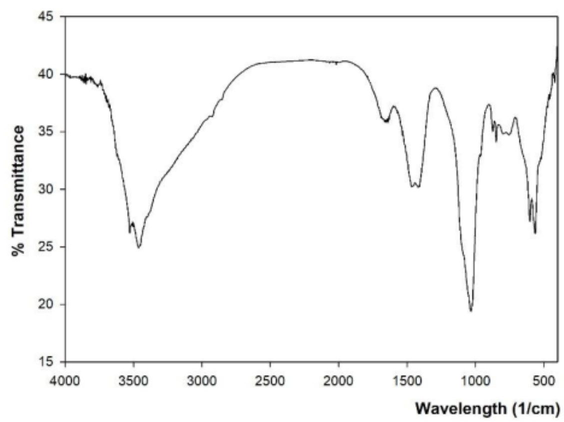

Figure 1. FTIR spectra of the CS/Mg/Al–LDH using 50% NaOH as solvent concentration (% DD of 97.40%)

Figure 1 shows the results of the FTIR spectra, where the spectral features of CS/Mg/Al–LDH were typical, as follows: 3462.34 cm^{-1} (O–H stretch overlapped with N–H stretch), featuring the vibration in the octahedral lattice, the hydroxyl group, and the interlayer anions, specially the band near 3500 cm^{-1} was attributed to the H–bonding stretching vibration in the brucite–like [13], 2924.18 and 2854.74 cm^{-1} (C–H stretch), 1649.19 cm^{-1} (C=O stretch), 1467.88 cm^{-1} (NH_2 bending), 1408.08 cm^{-1} (C–H bending), 1382.02 cm^{-1} (NO_3^- bending), the spectrum of LDH with interlayer anion of nitrate [13], and 1022.70 cm^{-1} (C–O stretch).The bond in lower wavelength spectrum (500 cm^{-1} to 800 cm^{-1}) corresponded to M–OH vibration and O–M–O stretching (where M were metal ions) [13]. Furthermore, Figure 1 also shows deacetylation of chitin using NaOH 50% (w/v) as solvent uptake group C=O at 1647 cm^{-1} was almost reduced and became chitosan [14], so that the process of deacetylation was obtained in a high grade chitosan. The degree of deacetylation of chitosan was determined based on calculations using a simple mathematical equation derived from Domszy and Robert with the Baxter method [15] obtained at a NaOH 50% (w/v) and at concentration of solvent around 90–98%.

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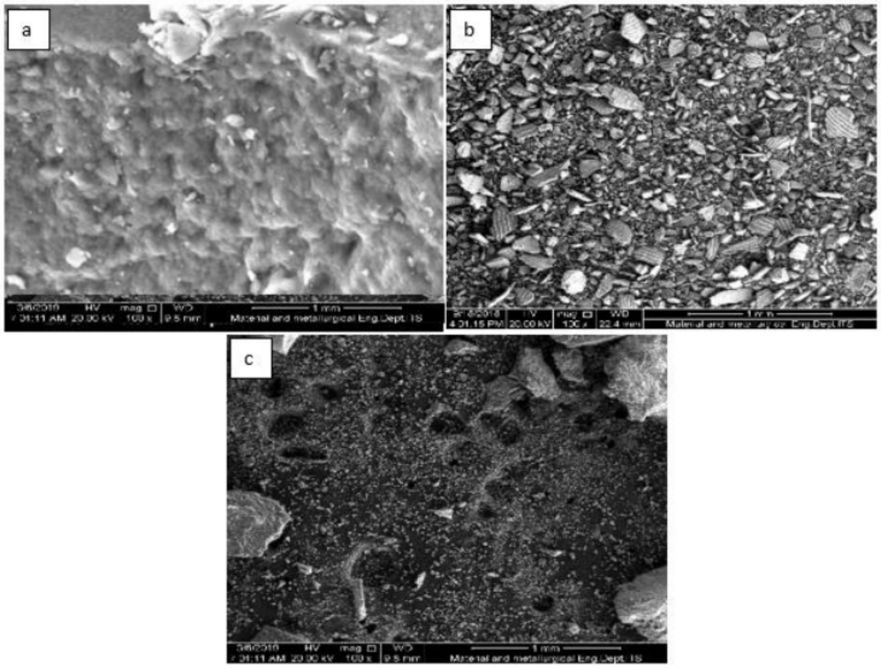

Figure 2. SEM images of Chitosan (a), Mg/Al–LDH (b) and chitosan/Mg/Al–LDH composite (CS/Mg/Al–LDH) (c).

SEM images of the chitosan (CS), Mg/Al LDH and chitosan/Mg/Al LDH (CS/Mg/Al–LDH) composite are shown in Figure 2. These micrographs confirmed an intercalation of CS into Mg/Al–LDH. The SEM images of CS/Mg/Al–LDH confirms the formation of sheet-like structure with a particle size around 1 μm and a heterogenous structure. However, the aggregation of some particles was also observed. The heterogeneous structure promotes the adsorption density efficiency through diffusion of the adsorbate onto the surface of the adsorbent [12].
Besides characterizing the functional group and structure morphology of CS/Mg/Al–LDH, XRF analysis method also measured the dominant elemental chemical contained in the adsorbent. It was confirmed that Mg, Al, Si and Ca elements were dominant compared to other elements (data not shown in this paper).

3.2. Batch Adsorption Studies
Figure 3 illustrates the effect of contact time on the adsorption of iron, turbidity, colour and measured pH change during adsorption process using CS/Mg/Al–LDH as adsorbent. During the first 60 minutes, adsorbents gained faster adsorption uptake capacity, and reached maximum saturation at 12 hours. Hence, 12 hours was fixed as the contact time for CS/Mg/Al–LDH adsorbent for further experiments in the adsorption process. In the beginning, the adsorption rates of iron, turbidity and colour percentage increased highly with increasing contact time, this might be reasonably explained by the presence of a huge vacant site on the adsorbents in the initial and the results, which clearly shows that the adsorption process was going up to equilibrium. Beyond 12 hours, there was no significant change recognized in the uptake capacity and this was perhaps because the surface of adsorbent was saturated. The uptake capacity of CS/Mg/Al–LDH was found to be more than 90%. Since CS/Mg/Al–LDH

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showed higher adsorption capacities, it seemed that pH change would have the same tendency of having no significant change after 12 hours of adsorption process.

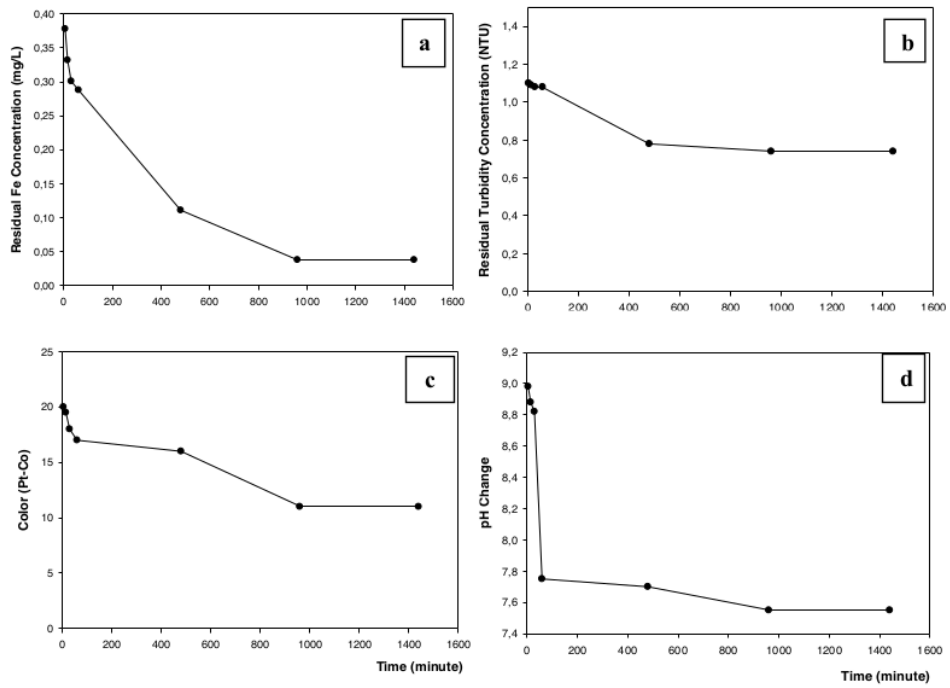

Figure 3. Adsorption rates of iron (a), turbidity (b), colour (c) and pH changes (d) at room temperature, stirring rates of 150 rpm, adsorbent dose of CS/Mg/Al-LDH of ca. 0.5 g/L.

The adsorption of iron (Fe), turbidity and colour was studied as a function of adsorbent dose at pH_e level 7,3±0,2. Shown in Figure 4, the uptake capacity increased with increasing doses and reached more than 90% at a dose of 3 g/L, and the remaining iron (Fe) concentration in the sample solution was 0.038 mg/L, turbidity 0.74 NTU and color 8 Pt-Co. The fact that uptake capacity increased with increasing adsorbent dose was because when the adsorbent dosage increases, the total surface area and the number of active sites of the adsorbent will also increase which will then increase uptake density capacity of iron, turbidity and colour in this batch adsorption experimental [16, 17].

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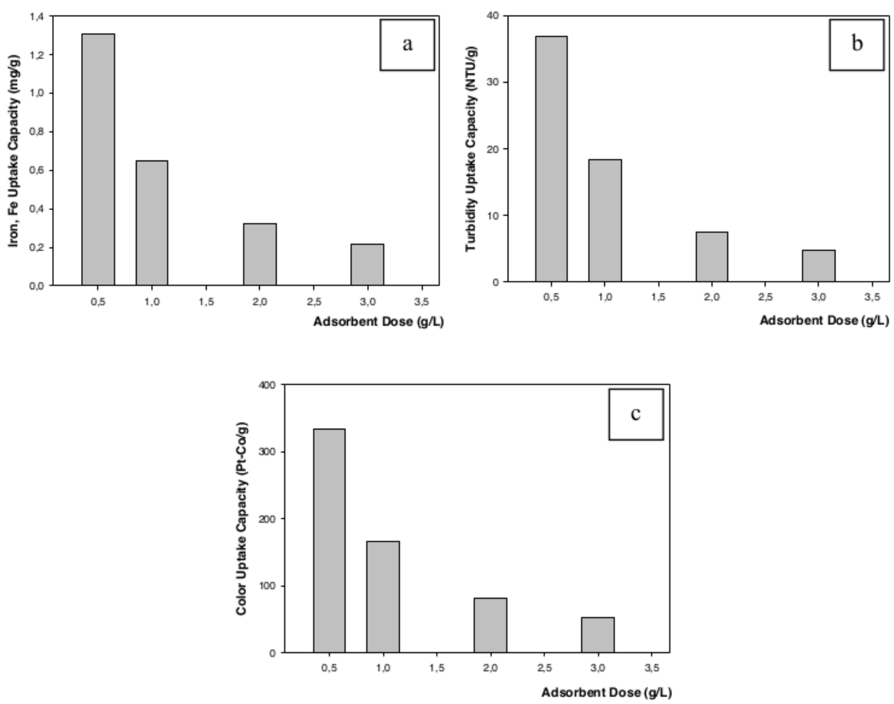

Figure 4. Adsorption uptake capacity of iron (a), turbidity (b) and color (c) at room temperature, stirring rates of 150 rpm, pH_e of 7,3±0,2 at various adsorbent dose of CS/Mg/Al-LDH.

4. Conclusions

Chitosan from fish scales as raw material of the composite had a deacetylation rate of around 90–96%. The physical characterization using SEM and FTIR showed that CS/Mg/Al-LDH had many different functional groups and a high specific surface area for adsorption processes. The XRF measurement results from the CS/Mg/Al-LDH indicated that the Mg, Al, Si and Ca elements were dominant in the sample and played a role in the sample adsorption process. The optimum condition for CS/Mg/Al-LDH as adsorbent in the treatment of raw water sources in municipal waterworks (PDAM Bandarmasih) by adsorption process yielded output water within the standard values as determined by the drinking water standard regulation in Indonesia with iron (Fe) at 0.038 mg/L, turbidity at 0.74 NTU and color at 8 Pt-Co at room temperature, stirring rate of 150 rpm, and adsorbent dose of CS/Mg/Al-LDH around 3 g/L.

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