Biopolymer of Chitosan from Fish Scales as Natural Coagulant for Groundwater Treatment

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Abstract—Chitosan, the de-acetylated chitin derivative, was evaluated for its ability to be used as a coagulant for Martapura groundwater treatment. This study is used chitosan derived from original fish scales of Kalimantans called Papuyu (Anabas testudineus) for the treatment of iron ion-containing Martapura groundwater through coagulation-flocculation method. The reduction efficiency of iron ion removed by coagulation-flocculation processes using chitosan from Papuyu fish scales is the main evaluating parameter. The obtained chitosan have been characterized and analyzed by Fourier transforms infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM). Using of the chitosan from Papuyu fish scales as coagulant at neutral pH and room temperature led to decreasing the groundwater iron concentration become 3.43 mg/L (around 71% removal). The result was then compare to the coagulation-flocculation treatment using the commercial chitosan from shrimps shell (93% deacetylated). Moreover, it found the coagulation-flocculation treatment using the chitosan from fish scales as coagulant more favor than the commercial one.

Keywords: chitosan, fish scales, biopolymer coagulant, coagulation, iron, groundwater

1. Introduction

Iron, one of the most common metal on earth, may present in groundwater due to the process of rain filtering through soil, rocks, and mineral even naturally nor caused by mining activity. Recently, based on observations of groundwater quality located in Martapura, South Kalimantan, Authors identifies that groundwater there containing iron (II) ion concentration is around 11.80 mg/L, pH of 5.4±0.2. The water quality is exceeding the permitted limit of World Health Organization (WHO), which is set a guideline value of 0.3 mg/L and pH of 6–8 (WHO 2011).

There have been several methods of iron removal applied from aqueous solutions including electro-coagulation, chemical precipitation, reverse osmosis, ion exchange, filtration, sand filtration, chemical reduction/oxidation, electrochemical precipitation, membrane filtration, solvent extraction, electrochemical deposition, adsorption, bioremediation, supercritical fluid extraction (Huang et al. 2012; Chaturvedi and Dave 2012). However, it is need to developing appropriate technology including low cost, low energy consumption and energy utilization, and minimize secondary wastes that are difficult to dispose of. Precipitation method by coagulation-flocculation processes has been found as promising technique in handling contaminated groundwater for potable water (Bordoloi, 2011). Coagulant types are often used include aluminium (III) sulphate, lime, ferrous (II) sulphate, poly aluminium chloride (PAC), and others.

Furthermore, it appears from the aforementioned investigations that most attention has been paid to approach the use of natural coagulants. These coagulants are often derived from food processing waste and are therefore non-toxic and of low cost. A more readily available natural coagulant is chitosan, which is typically derived from arthropods, the carapace of crustaceans as well as certain fungi and yeasts (Fabris et al. 2010). Besides, chitosan can also be obtained from fish scales.
The production of fishery aquaculture in Indonesia in year of 2015 reached 10.07 million tons. It is an increase of 3.98% compared to production in 2014 of 9.69 million tons, with an average increase of from 2010 - 2014 is 14.46%. South Kalimantan itself contributes to the average annual cultivation of 89.260 thousand tons of aquaculture, almost 1% of Indonesia's national production (Ministry of Marine Affairs and Fisheries, 2015).

Fish Wastes are available in large quantities amount in the environment, and then has the potential to produce value-added products. According to current research, fishery wastes are a useful material that can be used as raw material for the manufacture of chitin and chitosan. Chitin and chitosan have high potential in new functional biomaterials in areas such as cosmetics, agriculture, food and biomedical and textile industries as chelating agents, industrial waste treatment and biotechnology applications (Lodhi et al., 2014). Papuyu fish (Anabas testudineus Bloch), one of the local fish species typical of South Kalimantan, which are often found in swamp area is used in this present study. Chitin will be extracted from Papuyu fish scales. The Chitin obtained is converted into more useful chitosan. Chitin and Chitosan obtained were characterized by using X-Ray diffractometry (XRD), X-Ray Fluorescence (XRF), Fourier Transform Infrared (FTIR), and Scanning electron microscopy (SEM) analysis.

The aim of this present work is to experimentally investigates the degree of deacetylation of chitosan obtained from Papuyu fish scales in the process of deacetylation of chitin and characterized the surface morphology of the obtained chitosan. This research was also to evaluate the effectiveness of chitosan from Papuyu fish scales for the efficiency and capacity of iron (Fe) ion removal, and then compared the result to chitosan commercial as a natural coagulant for the groundwater treatment.

2. Methodology

2.1. Preparation of chitosan from Papuyu fish scales

Chitosan will be extracted by No and Meyers (1997) method with some modifications. Chitosan synthesis involves three major steps such as deproteinization (using NaOH), demineralization (using HCl) and deacetylated. Deproteination step was carried out with 3.5% NaOH 1:5 (w/v) at 65°C for 2 hours, then washed with deionized water until the sample reached neutral pH and dried at 65°C for 24 hours. Demineralization with 1 N HCl solution at room temperature with a ratio of 1:15 (w/v) for 30 minutes. The excess HCl present in the chitin sample was removed by thorough washing, washed with deionized water to neutral pH and dried at 65°C for 24 hours to yield chitin. Deacetylation process was prepared by alkali treatment of the chitin using NaOH 30, 40, 50, and 60% (w/v) for 4 hours at 100°C with a ratio of 1:10 (w/v). The formed chitosan were filtered, washed with deionized water to neutral pH and dried at 65°C for 24 hours.

Field-emission scanning electron microscopy (FESEM, JOEL JSM-6500F) with energy-dispersive X-ray spectroscopy (EDAX), was used for the surface morphology, Fourier transform infrared spectrometry (Bio-rad, Digitlab FTS-3500) was used for identified the surface functional groups of the chitosan from Papuyu fish scale.

The degree of deacetylation (DD) of chitosan was determined by a Fourier Transform IR spectrum using the Fourier transform infrared spectroscopy. The FTIR analysis method is frequently used for a qualitative evaluation and comparison studies, and it method better than that by the elemental analysis (Kumari et al. 2015). The DD of the chitosan was calculated using the following equation which was proposed by (Domszy and Roberts 1985):

\[
%DD = 100 - \left( \frac{A_{1665}}{A_{3450}} \right) \times \frac{100}{1.33} \tag{1}
\]
2.2 Coagulation-flocculation process for groundwater treatment

Jar test procedure was used to examine the efficiency of chitosan from Papuyu fish scales as coagulant and flocculant for the treatment of sample of the groundwater. The coagulant chitosan from Papuyu fish scales and chitosan commercial created in a concentration of 1% (w/v) at a dose of (20 – 100 mg/L) using a solution of 1% (v/v) CH₃COOH. The coagulation-flocculation tests were conducted on the collected groundwater sample in 500 mL beaker glass at room temperature and pH of 6±0.2. The two coagulants were added in separated experiments. The Coagulation and flocculation processes using the Jar test on rapid stirring rate of 200 rpm for 3 minutes, slow stirring rate of 50 rpm for 10 minutes and precipitation of a hour for settling time. Then the samples solution analyzed for residual of iron (Fe) using inductively coupled plasma atomic emission spectrophotometer (ICP-AES JY2000 2, Horiba Jobin Yvon). Jar test to determine removal efficiency of iron (Fe) ion were conducted in triplicate.

3. Results

Preparation of chitosan through three steps subsequent processes i.e. deproteination, demineralization and deacetylation are experimentally conducted in the laboratory. The yields obtained from each step of the processes are presented in Table 1.

| The Step          | Initial Mass (g) | Yield (g) | Percentage of yield (%) |
|-------------------|------------------|-----------|-------------------------|
| Deproteination    | 252              | 171       | 67.86                   |
| Demineralization  | 171              | 28,2      | 16.49                   |
| Deacetylation     | 28.2             | 3.7       | 13.12                   |

Figure 1 shown the results of the analysis of the degree of deacetylation chitosan from Papuyu fish scales using solvent concentration of 60% NaOH with FTIR analysis.
According to (Kumari et al. 2015), acetylamino group deacetylation of chitin in the process is converted into the amino group is characterized by reduction of C=O group absorption of molecules on FTIR spectrum.

Figure 2. The SEM analysis of (a) Papuyu fish scale; (b) Powder of Papuyu fish scale; and (c) Chitosan from Papuyu fish scales
Based on Figure 1 deacetylation of chitin using solvent NaOH 60% (w/v) uptake group C=O is almost reduction, so that the process of deacetylation is perfect. The degree of deacetylation of chitosan calculated based on calculations using the mathematical simple derived by Domszy and Robert with the Baxter method obtained at a concentration of solvent NaOH 30, 40, 50, and 60 % (w/v) in the amount of 88.82, 94.39, 95.06 and 97.48 %, respectively.

Figure 2 characterization using SEM analysis shown that surface morphology Papuyu fish scales into chitosan are changed. Papuyu fish scales have a closed surface of the particles, the particles pulverized fish scales be open and not in the regular form, appears to have fibrillar and the granular structure on the surface. While chitosan has a smoother surface and the fibers structures are seen with a fractured appearance.

The number of epidermal showed that the chitosan-containing collagen which is a protein fiber that gives strength and flexibility to act as a natural coagulant. It was also observed that the biopolymer of chitosan from Papuyu fish scale has becomes porous and fibril structures (G Zaku et al. 2011; Kumari et al. 2015). The percentage removal of iron (III) ion using chitosan from Papuyu fish scales and chitosan commercial as coagulant depicted in Figure 3.

![Figure 3. Percentage of Iron (Fe) removed with various coagulant doses (mg /L) of chitosan from Papuyu scales and commercial one.](image)

Chitosan coagulant dose of 40 and 50 mg/L has optimum condition as a coagulant and flocculant, meaning that the concentration of particles and the formation of the destabilization of flocculants has formed. Based on Figure3, chitosan from Papuyu fish scales decreased the concentration of ferrous metals. This is due to chitosan from Papuyu fish scales has a degree of deacetylation is higher than chitosan commercial. Chitosan from Papuyu fish scales has a degree of deacetylation of 97.40%, while chitosan commercial of 93.80%. According Kasvaei (1998), the ability to form flocks of chitosan in the coagulation-flocculation process is influenced by the degree of deacetylation of the chitosan-making process. Then also at this solution pH of 6±0.2, the chitosan amino groups are expected to be deprotonated and therefore have negative charge density and electrostatic interaction to iron (Fe) ion (Fabris et al. 2010).

Used of the chitosan from Papuyu fish scales as coagulant at neutral pH, coagulant dose of 40 mg/L, and room temperature led to decreasing the groundwater iron concentration become 3.43 mg/L as shown in Figure 4 compared to the commercial chitosan that only decreasing iron (Fe) concentration become 7.28 mg/L (around 38% removal).
Figure 4. Residual of iron (Fe) re with various coagulant doses (mg /L) of chitosan from Papuyu scales and commercial one.

4. Conclusions

These properties, combined with its non-toxicity, make the chitosan from Papuyu fish scales most favour and the better substitute to the commercial and conventional synthetic polyelectrolites used so far. The degree deacetylation of obtained chitosan from Papuyu fish scales is higher than commercial chitosan. So that chitosan from Papuyu fish scales is being potential to be applied as natural coagulant in a coagulation/flocculation for removal iron (II) ion in groundwater treatment and substitute for aluminium (III) sulphate, ferric (III) chloride, polyaluminium chloride (PAC), etc. Using of the chitosan from Papuyu fish scales as coagulant at neutral pH and room temperature led to decreasing the groundwater iron (Fe) concentration become 3.43 mg/L (around 71% removal). However, it is also taking into account that the iron (Fe) retained in the sediment formed is worth considering minimizing residual Fe concentration below the standard value.

5. Acknowledgment

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