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

Biopolimer Kitosan dari Sisik Ikan Sebagai Koagulant Alami untuk Pengolahan Air Tanah Terkontaminasi Besi

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Abstract

Chitosan, the de-acetylated chitin derivative, was evaluated for its ability as a natural coagulant for Martapura groundwater treatment. This study used chitosan derived from original fish scales of Kalimantan called Papuyu (*Anabas testudineus*) for the treatment of Martapura groundwatercontaining iron ion through coagulation-flocculation method. The reduction efficiency of iron ion removed by coagulation-flocculation processes using chitosan from Papuyu fish scales is the primary evaluating parameter. The obtained chitosan have been characterized and analyzed by Fourier transforms infrared spectroscopy (FTIR), X-ray Fluroscence (XRF) and Scanning electron microscopy (SEM). Using of the chitosan from Papuyu fish scales (97.40% deacetylated) as coagulant at neutral pH and room temperature led to decreasing the groundwater iron concentration from 11.80 mg/L 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 (93.80% deacetylated). Moreover, its found the coagulation-flocculation treatment using the chitosan from fish scales as coagulant more favor than the commercial one.

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

Abstrak

Kitosan, turunan kitin terdeasetilasi, telah diuji kemampuannya sebagai koagulan alami dalam pengolahan air sumur Martapura. Penelitian ini menggunakan koagulan dari sisik ikan khas Kalimantan yang dikenal sebagai Papuyu (*Anabas testudineus*) untuk penurunan kandungan besi yang mencemari air sungai Martapura dengan proses koagulasi-flokulasi. Kitosan dari sisik ikan Papuyu dikarakterisasi dan dianalisa menggunakan *Fourier transforms infrared spectroscopy* (FTIR), *X-ray Fluroscence* (XRF) dan *Scanning electron microscopy* (SEM). Kitosan dari sisik ikan Papuyu ini pada kondisi netral pH 7 dan suhu kamar mampu menurunkan konsentrasi besi menjadi 3,43 mg/L dari kondisi awal sekitar 11,80 mg/L (dengan efisiensi penurunan sekitar 71%). Hasil yang diperoleh dibandingkan dengan kitosan komersial dari kulit udang (yang mengandung derajat deasetilasi 93,80%) dan diperoleh bahwa kitosan dari sisik ikan Papuyu lebih baik daripada kitosan komersial.

Kata kunci: koagulan, kitosan, sisik ikan, air sumur, besi

1. Introduction

Iron, one of the most common metal on earth, may present in groundwater because of the process of rain filtering through soil, rocks, and mineral even naturally or caused by mining activity. Recently, based on observations of groundwater quality located in Martapura, South Kalimantan, the 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 2017).

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 (Chaturvedi and Dave, 2012; Huang et al., 2012). However, it is need to developing appropriate technology including low cost, low energy consumption and energy utilization, and minimized secondary wastes that are difficult to dispose of.

Precipitation method by coagulation-flocculation processes has been found as a promising technique in handling contaminated groundwater for potable water (Bordoloi et al., 2013). 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 Indonesian in the year of 2015 reached 10.07 million tons. It is an increased 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 waste is 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 (Chen et al., 2018; Lodhi et al., 2014; Oladoja, 2015).

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 Fluorescence (XRF), Fourier Transform Infrared (FTIR), and Scanning electron microscopy (SEM) analysis.

The aims 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 (III) ion removal, and then compared the result to chitosan commercial as a natural coagulant for the groundwater treatment.

2.Methodology

2.1. Chitosan Preparation from Papuyu Fish Scales

Chitosan is extracted by (No and Meyers, 1995) 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 wateruntil 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 was filtered, washed with deionized water to neutral pH and dried at 65°C for 24 hours.

2.2. Characterization of Chitosan from Papuyu Fish Scales

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, Digilab FTS-3500) was used for identifying 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 its method better than that by the elemental analysis (Kumari et al., 2015). The DD of the chitosan was calculated by drawing a vertical line in the spectrum resulting from FTIR analysis at a wavelength of 1655 cm^{-1} and 3450 cm^{-1}. Withdrawal of the line according to the following equation which was proposed by (Domszy and Roberts, 1985) based on the Baxter Method:

$$\%DD=100-\left[\left(\frac{A_{1665}}{A_{3450}}\right)\times\frac{100}{1.33}\right] \quad (1)$$

Where is DD is degree of deacetylation, A_{1665} is absorbance in wavelength of 1665 cm^{-1}, A_{3450} is absorbance in wavelength of 3450 cm^{-1}, 1.33 is constant ratio of A_{1665}/A_{3450}.

2.3. 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 the sample of the groundwater. The initial iron (III) in the sample is around 11.80 mg/L. The coagulant chitosan from Papuyu fish scales and chitosan commercial were used in this study ranged from 2% to 10% (w/v), which correspond to a dose range of 20–100 mg/Lof chitosan per liter of 1% (v/v) acetic acid solution (CH_3COOH).

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 an hour for settling time. Then the samples solution analyzed for residual of iron (III) using inductively coupled plasma atomic emission spectrophotometer (ICP-AES JY2000 2, Horiba Jobin Yvon). Jar test to determine removal efficiency of iron (III) ion were conducted in triplicate. The removal rate of iron ions obtained according to the following equation:

$$\text{Removal }(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

Where is C_o is initial concentration (mg/L), C_e is final concentration (mg/L).

3. Results and Discussion

3.1. Characterization of Chitosan

Preparation of chitosan are experimentally conducted in the laboratory through three steps subsequent processes i.e. deproteination, demineralization and deacetylation. The yields obtained from each step of the processes are presented in Table1.

Deproteination process will reduce the mass of raw fish scales using a solution of NaOH 3.5% (w/v), which is proteins on the fish scales will be dissolved with NaOH, due to a protein derived from a Papuyu fish scales as shown in Table 1.

Table 1. The yield per steps of chitosan from Papuyu fish scales

The step	Initial mass (g)	Yield(g)	Persentase ofyield(%)
Deproteination	252	171	67.85
Demineralization	171	28,2	16.49
Deacetylation	28.2	3.7	13.12

The obtained of mass reduction around 67.85% during 24 hours deproteination process. (Synowiecki and Al-Khateeb, 2003) in their research got the protein content is around 61.6%. In the demineralization process, a mass reduction due to the removal of inorganic compounds found in Papuyu fish scales in the form of minerals. The mineral content in crustacean is primarily in the form of $CaCO_3$ and also $Ca_3(PO_4)_2$ in small quantities (Abdulkarim et al., 2013; Synowiecki and Al-Khateeb, 2003). The process of demineralization occurs in a mass reduction of 16.49%. Once isolated, the chitin can be processed into chitosan by deacetylation process. The purpose of deacetylation of chitin is to remove the acetyl groups that exist in chitin. Deacetylation is the process of converting an acetyl group ($NHCOCH_3$) into an amine group ($-NH_2$) (Abdulkarim et al., 2013).

Deacetylation reaction of chitin is essentially an amide hydrolysis reaction of β-(1-4)-2-acetamide-2-deoxy-D-glucose with concentrated NaOH solution. The mass reduction in the process of deacetylation is around 13.12%. This mass reduction occurs because of the transformation of the acetyl group bonded to a nitrogen atom into an amine group (the removal of acetyl groups), wherein the molecular weight of the acetyl group bonded to the nitrogen atom that is greater than the amine group. It indicates when a higher degree of deacetylation (some acetyl groups replaced), high the mass reduction occurred.

Figure 1 is 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. The spectral features ofchitosan from Papuyu fish scales (Figure 1) are as follows: 3329.58 cm^{-1}(O–H stretch overlapped with N–H stretch), 2916.96 and 2878 cm^{-1} (C–H stretch), 1647 cm^{-1} (C=O stretch), 1575.89 cm^{-1} (NH_2bending), 1419.69 cm^{-1}(C–H bending), 1156.56 cm^{-1} (bridge C–O–C stretch) and 1022.70 cm^{-1} (C–O stretch).

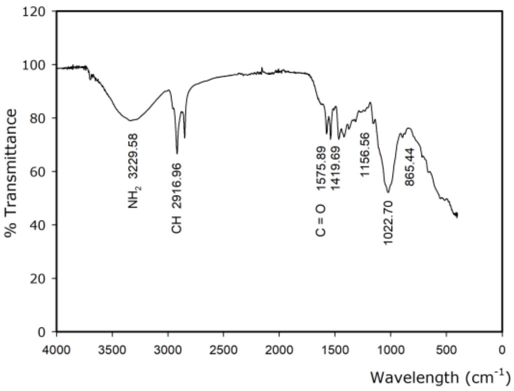

Figure 1. FTIR spectra of the chitosan from Papuyu fish scales using solvent concentration of 60% NaOH (% DD of 97.40%)

Based on Figure 1., deacetylation of chitin using solvent NaOH 60% (w/v) uptake group C=O at 1647 cm^{-1} is almost reduction become chitosan (Kumari et al., 2015), so that the process of deacetylation is obtained high grade of chitosan. The degree of deacetylation of chitosan calculated based on calculations using the mathematical simple derived by (Domszy and Roberts, 1985) with the Baxter method obtained at a concentration of solvent NaOH 30, 40, 50, and 60 % (w/v) in the amount of 88.80, 94.40, 95.10 and 97.40 %, respectively. Furthermore, the degree of deacetylation shows the percentage uptake ratio N-H group with C=O group of the amide. The comparison could show changes in the quantity of C=O group of the amide. The process of deacetylation of the chitosan resulting in a reduced amount of C=O group of amide so absorbance C=O group of amide will also decrease.

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 notin 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.

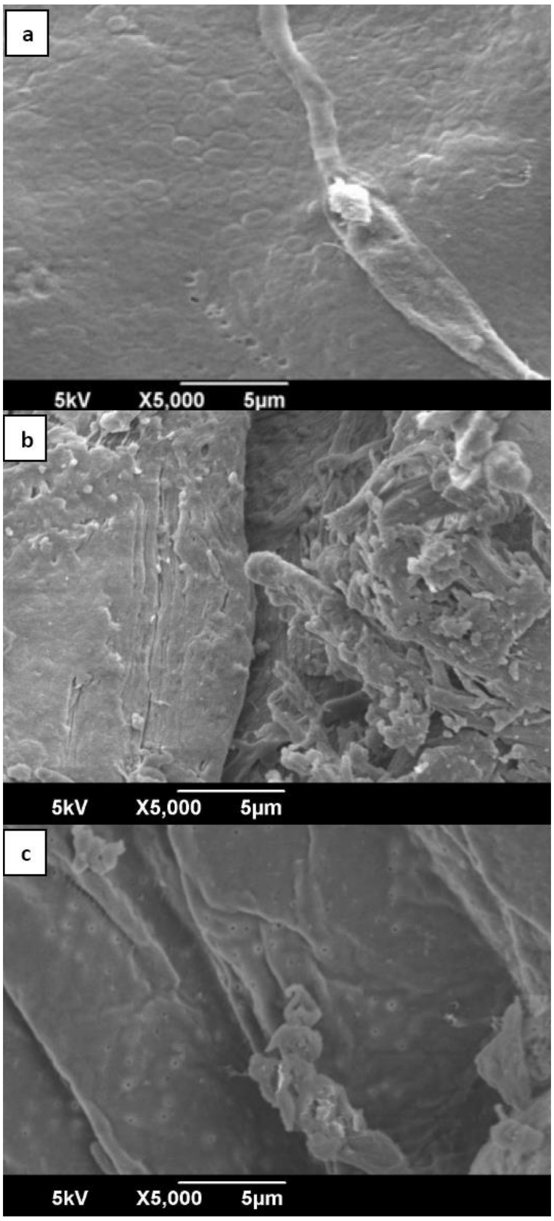

Figure 2. The SEM analysis of (a) Papuyu fish scale; (b) Powder of Papuyu fish scale; and (c) Chitosan from Papuyu fish scales

It was also observed that the biopolymer of chitosan from Papuyu fish scale has become porous and fibril structures (Zaku et al., 2011; Kumari et al., 2015). The EDX analysis (not shown in this paper) was confirmed the presence of C, N, and O in the chitosan (Lewandowska et al., 2014) beside Si and Ca.

XRF analysis can be using to conclude the identity and quantities of the elements in samples. It is appropriate for determination of elemental chemical concentrations in samples (Chang et al., 2006). Even in this research, the chitosan using as natural coagulant for iron-contaminated groundwater treatment, furthermore chitosan is also counted as natural adsorbent results from the presence of amine and hydroxyl groups (Chen et al., 2018; Ngwabebhoh et al., 2016) besided its chemical composition as shown in Table 2. that have contribution for iron removal.

Table 2. Chemical composition of Chitosan from fish scale measured by XRF

Sample	Chemical composition (percentage of mass, %)						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	P_2O_5	ZnO	Other
Chitosan	14.0	5.0	25.0	44.9	6.8	1.9	2.4

3.2. Coagulation-Flocculation of Iron-Contaminated Groundwater Treatment

The percentage removal of iron (III) ion using chitosan from Papuyu fish scales and chitosan commercial as coagulant depicted in Figure 3. Chitosan coagulant dose of 40 and 50 mg/L has the optimum condition as a coagulant and flocculant, meaning that the concentration of particles and the formation of the destabilization of flocculants has formed.

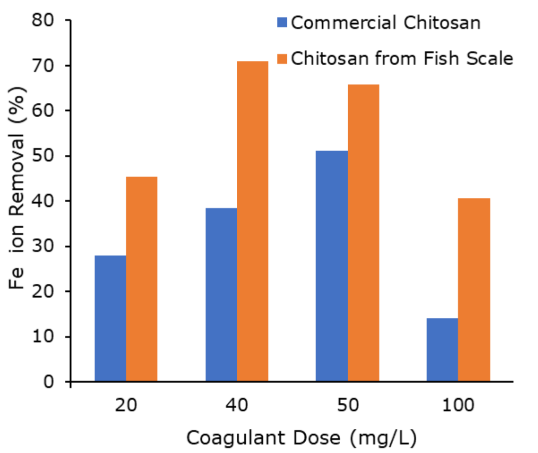

Figure 3. Percentage of Iron (III) removed with various coagulant doses (mg /L) of chitosan from Papuyu scales and commercial one.

Based on Figure 3, 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 to 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).

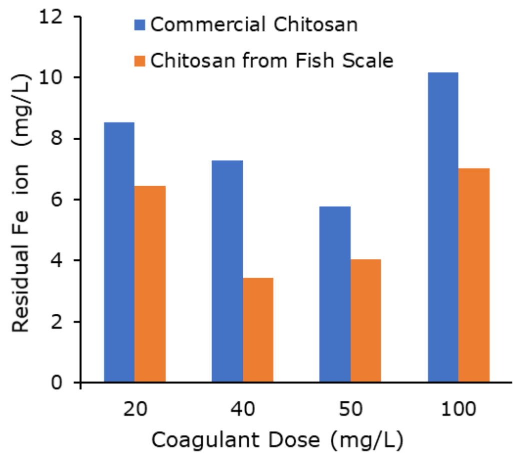

Figure 4. Residual of iron (III) using various coagulant doses (mg /L) of chitosan from Papuyu scales and commercial one.

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 (around 71% removal) as shown in Figure 4 compared to the commercial chitosan that only decreasing iron (Fe) concentration become 7.28 mg/L (around 38% removal). Chitosan tends to neutral charged particles in the supernatant solution if the solution had lower alkalinity contains. The presence of alkalinity and calcium ions in the solution indicate bridging mechanism involved in binding the particles to form agglomerates (Ang et al., 2016).

4. Conclusions

These biopolymer chitosan properties, combined with its non-toxicity, make the chitosan from Papuyu fish scales most favor and the better substitute to the commercial and conventional synthetic polyelectrolytes used so far. The degree deacetylation of obtained chitosan from Papuyu fish scales (around 97.40%) is higher than commercial chitosan (93.80%). So that chitosan from Papuyu fish scales is being potential to be applied as the 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 fromPapuyufish scales as coagulant at neutral pH and room temperature led to decreasing the groundwater iron (Fe) concentration from 11.80 mg/L become 3.43 mg/L (around 71% removal). However, it is also taking into account that the iron (III) retained in the sediment formed is worth considering minimizing residual Fe concentration below the standard value.

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