The effect of deproteinization temperature on chitosan extraction for iron metal ions adsorption: Case study in Bangka post tin mining water

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Abstract. This study aims to analyze the effect of deproteination temperature on the chitosan adsorption for iron metal ions in Banga post tin mining water. Extraction of chitosan was carried out in four steps: deproteinization, demineralization, decolorization and deacetylation of chitin. The effect of deproteinization temperature on deacetylation process was studied. The results shown that the increase of deproteinization from 30°C to 90°C causes the decrease of chitosan deacetylation degree (DD): 65.72%; 64.31% and 63.75% respectively. The increase of deproteinization temperature triggers excess depolymerization which damages the chitin structure so that it has a negative effect on the chitosan DD. The metal content of iron in post tin mining water sample this study reached 6.1 ppm. Adsorption of chitosan on iron metal ions reduced the dissolved levels reaching an average of 99.67% from the initial content. The adsorption of iron lead by chelation mechanism. The reaction of chitosan with iron metal ion lead the formation of complex compounds with chitosan as a ligand and metal ions as the central ion. Based on the ligand strength series in spectrochemistry, the hydroxyl functional group is to the left of the amine group, so that the amine group is stronger than the hydroxyl group in adsorbing metal ions. It is more likely to predict that the valency forces through the sharing of electrons between transition metal cations and adsorbent are the adsorption behaviour may involve.

1. Introduction
The Province of Bangka Belitung Islands is a province known as the largest tin producer in Indonesia and is the main backbone of the province's economy [1]. As mining activities expand every year, this will threaten the sustainability of the surrounding environment [2]. Empowerment of ex-mining areas is one of the strategic issues that has attracted many researchers from various disciplines to study. Starting from reclamation activities to utilization of former puddles as a medium for fish cultivation [3].

Water pollution by toxic metals from tin mining activities remains a serious environmental problem and can threaten the living systems. The content of heavy metals in water is a very important parameter. This is because if the water as a culture medium contains heavy metals, it is possible that the heavy metals can be absorbed into the biota body and accumulate so that it is dangerous for human consumption [4]. The biomagnification process allows heavy metals to accumulate in the biota body.
One of the efforts to remediate the post tin mining water sample from an inactive tin mining pond using adsorbent material that can absorb heavy metals [5-8]. This material functions to bind dissolved metal cations with anions lead chelation mechanism so that dissolved metal levels will decrease [9]. Chitosan is one of the adsorbent materials that has been developed and is in great demand. This is because chitosan has several advantages including environmentally friendly (leaving no pollutant emissions), abundant sources (generally from crustacean shells) and non-toxic [10-13]. Chitin is a chitosan precursor compound that is widely contained in crustacean shells, especially shrimp and lobster [14-15].

In Bangka Belitung province, easily can find the crustacean processing industry: shrimp, lobster, and crab as a low-cost sorbent which is abundant for chitosan product. Chitosan has been reported to have high potential for adsorption of metal ions. In this work, we report effect of deproteinization temperature on deacetylation degree of chitosan and the effectiveness of the iron metal ions sorption onto chitosan in the post tin mining water sample from an inactive tin mining pond in the Bangka Island area.

2. Methods

2.1. Materials

Samples of chitosan were extracted at previous work [16] in variation of deproteinization temperature and the degree of deacetylation of each sample defined by an IR method shown in Table 1.

| Sample | Deproteinization temperature (°C) | Degree of deacetylation (%) |
|--------|----------------------------------|----------------------------|
| 1.     | 30                               | 65.72                      |
| 2.     | 60                               | 64.31                      |
| 3.     | 90                               | 63.75                      |

In this study, the post tin mining water sample was obtained from an inactive tin mining pond in the Bangka Island area.

2.2. Adsorption experiments

The adsorption experiments procedure conducted by reacting the chitosan in the post tin mining water sample with a ratio of 1: 100 (w / v) and stirred by a magnetic stirrer for about 5 min at room temperature. After 30 minutes, the water is filtered to separate the chitosan deposits. The effectiveness of the iron metal ions sorption onto chitosan in water sample was analyzed using an atomic absorption spectrophotometer (ICE 3000 Model) with a detection limit of 0.0001 ppm at wavelength 248 nm before and after treatment.

3. Results and discussion

The heavy metal content of the post tin mining water sample was obtained from an inactive tin mining pond in the Bangka Island area is shown in Table 2.

| The heavy metal | Content (ppm) | Water quality standards (ppm) |
|----------------|---------------|-----------------------------|
| Fe             | 6.10          | 1.00                        |
| Zn             | 1.20          | 15                          |
| Pb             | 0.36          | 0.05                        |
| Cu             | 0.32          | 0.02                        |
Based on Table 2, the heavy metal content from water sample consists of Fe, Zn, Pb and Cu. The content of Fe, Pb and Cu have higher level than the minimum water quality standards from the Minister of Health Regulation No. 32 of 2017. While the Zn content is lower than water quality standard regulation. Especially the iron content of water sample has about six times than the minimum water quality standards from the Minister of Health Regulation No. 32 of 2017. It means that the water sample cannot be used before water treatment to reduce iron content done. Iron are mainly present as two oxidation states in natural water [17]. In Fe (II), iron are essential micronutrients for organism and plants. However, it become toxic at higher levels [18].

The effect of deproteinization temperatures on the adsorption of iron metal ions by chitosan shown in Table 3. As explain in previous work [16], the increment of deproteinization temperature causes the the deacetylation degree of chitosan decreased. It caused by an exceeded depolymerization reaction take placed as increment temperature which damages the chitin structure.

| Sample | Iron content (ppm) |
|--------|-------------------|
|        | Before | After |
| 1      | 6.10   | 0.010 |
| 2      | 0.02   | 0.020 |
| 3      | 0.03   | 0.030 |

The adsorption of iron lead by chelation mechanism. The increment of deacetylation degree of chitosan caused more amine groups (-NH₂) as chelating sites formed so that the ability of chitosan to bind iron metal ions is greater [19]. Meanwhile, the reaction of chitosan with iron metal ion lead the formation of complex compounds with chitosan as a ligand and metal ions as the central ion. Based on the ligand strength series in spectrochemistry, the hydroxyl functional group is to the left of the amine group, so that the amine group is stronger than the hydroxyl group in adsorbing metal ions [18-19].

The iron adsorption onto chitosan after adsorption treatment increased significantly. It may be caused by electron donors from the amine groups (-NH₂) on the chitosan chain. Dative bonds with transition metal ions established by the nitrogen electrons present the amine groups. It is more likely to predict that the valency forces through the sharing of electrons between transition metal cations and adsorbent are the adsorption behaviour may involve [20-21].

4. Conclusion
The increment of temperature deproteinization caused the deacetylation degree of chitosan decreased. The increment of deacetylation degree of chitosan caused more amine groups (-NH₂) as chelating sites formed so that the ability of chitosan to bind iron metal ions is greater. The adsorption of iron lead by chelation mechanism. The reaction of chitosan with iron metal ion lead the formation of complex compounds with chitosan as a ligand and metal ions as the central ion. Based on the ligand strength series in spectrochemistry, the hydroxyl functional group is to the left of the amine group, so that the amine group is stronger than the hydroxyl group in adsorbing metal ions. It is more likely to predict that the valency forces through the sharing of electrons between transition metal cations and adsorbent are the adsorption behaviour may involve.

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