The Adsorption Efficiency of Iron from Post-Tin Mining Water using Nanomagnetic Fe₃O₄/Chitosan Portunus pelagicus shells

E Julianti¹, A Samsiar¹, R N Siregar² and V A Fabiani¹*

¹Department of Chemistry, Faculty of Engineering, Universitas Bangka Belitung, Kampus Terpadu UBB, Balunijuk, Kepulauan Bangka Belitung, 33172, Indonesia.
²Department of Physics, Institut Teknologi Sumatera, Jl. Terusan Ryacudu, Jati Agung, Lampung Selatan, 35365, Indonesia.

*Corresponding author: verryandre89@gmail.com

Abstract. Adsorption was carried out on the water of post tin mining using nanomagnetic Fe₃O₄/chitosan from Portunus pelagicus shells. Nanomagnetic Fe₃O₄/Chitosan was prepared for iron adsorption. The nanomagnetic Fe₃O₄ was characterized through XRD and chitosan was characterized through FTIR. The concentration of Fe in post tin mining water is 6.1 ppm. This study varied the mass of Fe₃O₄ and stirring time. The adsorption results were analyzed by AAS and obtained the largest adsorption efficiency (96.72%) at stirring 30 minutes with a mass of Fe₃O₄ of 120 mg.

1. Introduction
At present tin mining activities continue and leave unresolved problems. The tin mining area causes the formation of post tin mining land with a very high level of heavy metal contamination. High metal content found in some water under the former tin mine on Bangka Island includes Fe, As, Al, Pb and Zn [1]. One of the heavy metals with high levels of contamination in the post tin mining water is iron ion. If accumulated in the human body can cause several dangerous pathological conditions such as oxidative stress, damage to organ systems and cause tissue damage in cells. [2].

Several methods for removing iron ions in wastewater have been carried out such as electrocoagulation [3], filtration/oxidation [4], ion exchange [5], aeration [6], biological treatment [7] and membrane technology [8]. In addition, physical-chemical treatment is also often used in removing heavy metals in water samples and aqueous solutions. [9]. Adsorbent material with a small size, large surface area and porous has a good ability to remove iron metals in water. [10], one of these materials are nanomagnetic. Nanoparticle magnetic (Fe₃O₄) has been shown to have high absorption of heavy metals from water [11].

Nanomagnetic (Fe₃O₄) has superior multifunctional properties such as low toxicity, small size, biocompatibility, superparamagnetic, and others. If compared with the remediation process that has been done in previous studies such as ion exchange, precipitation, coagulation, reverse osmosis and electrolysis, nanomagnetics have magnetic properties with high removal rates for contaminants, high adsorption efficiency, fast, and easy to separate adsorbents from solutions through magnetic fields [12]. However, on the other hand nanomagnetic Fe₃O₄ tends to be unstable and easily oxidized so that a composite is needed to overcome this. One of the composites used is chitosan polymer as a binder of...
Fe₃O₄ which aims to keep Fe₃O₄ stable, not easily oxidized, and not form aggregates. Chitosan is also known as toxic chelating metals. Powder or chitosan solution can eliminate or reduce metal or metal ions found in river water, sea water and waste water [13].

In this study, nanomagnetic Fe₃O₄/Chitosan from Portunus pelagicus shells was prepared for iron ion adsorption. The nanomagnetic Fe₃O₄ was characterized through XRD and chitosan was characterized through FTIR. This study varied the mass of Fe₃O₄ and stirring time. The adsorption results were analyzed by AAS.

2. Research methods

2.1 Isolation of chitosan from Portunus pelagicus shells
The initial preparation of chitosan from the Portunus pelagicus shell is by washing the shell under running water until it is brushed clean and dried under the sun then mechanically destined to become powder, the last step sieved with a size of 100 mesh. The steps of making chitosan include deproteination, demineralization and deasetilation. Chitosan was analyzed by FTIR.

2.2 Synthesis of nanomagnetic-chitosan
The first step is to weigh Fe₃O₄ nanoparticles according to the specified variation. Then make 1% chitosan solution by adding it with acetic acid. Fe₃O₄ nanoparticles mixed with 1% chitosan solution were stirred while adding a drop by setting an emulsifying solution containing 15 ml paraffin and 0.25 mL CMC 1%. Stir for 5 hours at room temperature. Then slowly add 5 mL of 37% formaldehyde and stir until the precipitate is formed. Then dried at 200 °C in the oven for 2 hours and stored in a dry place. Nanomagnetics was analyzed by XRD [14].

2.3 Adsorption
The composition of the mixed magnetic-chitosan nanoparticles is the number of magnetic nanoparticles. Variations used are 75 mg, 95 mg, 105 mg and 120 mg. After the mixture with variations in composition, magnetic chitosan nanoparticles were made into the post tin mining water. Stirring time variations are 30, 40 and 50 minutes. Then analyzed by atomic absorption spectrometer (AAS) [14].

3. Result and Discussion

3.1 Characteristics of nanomagnetic Fe₃O₄
The source of Fe₃O₄ used in nanomagnetic-chitosan synthesis comes from commercial materials that have been synthesized. To ensure the Fe₃O₄ phase formed, XRD analysis was then carried out.
Figure 1. XRD pattern of Fe$_3$O$_4$ (red) and Fe$_3$O$_4$ standard (blue)

The crystalline phase is indicated by the presence of diffraction peaks. The phase identification process is based on matching data from measured diffraction peaks with a database. The peaks that present Fe$_3$O$_4$ compounds are shown in Figure 1, namely at position 2$\theta$ equal to 30,10$^\circ$, 35,47$^\circ$, 43,13$^\circ$, 56,97$^\circ$, 62,60$^\circ$. Furthermore, particle size can be analyzed with the Scherrer formula and obtained an average size of 28.29 nm (Table 1).

![Equation](1)

$D = \frac{K \lambda}{\beta \cos \theta}$

where:
- $D =$ particle size
- $\lambda =$ wavenumber Cu-K$\alpha$ (1.5406 Å)
- $\theta =$ bragg angle (rad)
- $K =$ shape factor (0.9)
- $\beta =$ FWHM (rad)

| 2$\theta$ (deg) | $\theta$ (rad) | FWHM (rad) | D (nm) |
|-----------------|----------------|-------------|--------|
| 30,10           | 0,2627         | 0,0053      | 26,78  |
| 35,47           | 0,3095         | 0,0053      | 27,15  |
| 43,13           | 0,3764         | 0,0053      | 27,81  |
| 56,97           | 0,4971         | 0,0053      | 29,42  |
| 62,60           | 0,5462         | 0,0053      | 30,27  |

Table 1. Results of Data Analysis of Fe$_3$O$_4$ Particle Size

Average particle size (D) 28,29
3.2 FTIR of Chitosan

In Figure 2, there is a typical absorption for chitosan which is found in wave numbers 3225-3412 cm\(^{-1}\) which show the presence of hydrogen bonds from the -OH group which overlap with the -NH range. The absorption peak at wave number 2916 cm\(^{-1}\) and 2866 cm\(^{-1}\) show asymmetrical stretching of CH (-CH\(_2\)-). Meanwhile, there is an absorption intensity with a weak intensity at the wave number 1643 cm\(^{-1}\) which shows stretching C=O (-NHCOCH\(_3\)-). The absorption peak at wave number 1030 cm\(^{-1}\) shows symmetrical stretching of C-O (-C-O-C-).

3.3 Efficiency of adsorption

Nanomagnetic Fe\(_3\)O\(_4\)/chitosan synthesized was applied as iron ion adsorbent. The source of the post tin mining water in this study comes from the newly formed land about five months after tin mining took place in Rebu villages, Bangka regency.

| Stirring time (minutes) | Composition of Fe\(_3\)O\(_4\) (mg) | 0 mg | 75 mg | 95 mg | 105 mg | 120 mg |
|-------------------------|-----------------------------------|------|-------|-------|--------|--------|
| 30                      | 0,83                              | 1,60 | 1,72  | 2,08  | 0,2    |
| 40                      | 1,22                              | 3,8  | 2,03  | 5,03  | 5,2    |
| 50                      | 1,00                              | 1,4  | 2,37  | 1,5   | 2,70   |

Based on table 2, it can be seen that the optimum conditions for the iron adsorption process occur in addition to 120 mg of Fe\(_3\)O\(_4\) with a stirring time of 30 minutes.

| Stirring time (minutes) | Composition of Fe\(_3\)O\(_4\) (mg) | 0 mg | 75 mg | 95 mg | 105 mg | 120 mg |
|-------------------------|-----------------------------------|------|-------|-------|--------|--------|
| 30                      | 86,40                             | 73,77| 71,80 | 65,90 | 96,72  |
| 40                      | 80,00                             | 37,70| 66,72 | 13,11 | 14,75  |
| 50                      | 83,61                             | 77,05| 61,15 | 75,41 | 55,74  |
Based on the AAS analysis, the concentration of iron in the post tin mining water is 6.1 ppm and this is very high for the required water content limit. Table 3 explain that the adsorption efficiency of iron reaches 96.72%. This shows that nanomagnetic Fe₃O₄/chitosan successfully adsorbs iron in the post tin mining water.

4. Conclusion

In this study chitosan-nanomagnetic synthesis was successfully carried out. XRD data shows that nanomagnetic has a crystalline phase Fe₃O₄ with an average particle size of 28.29 nm. The optimum condition of iron adsorption in post tin mining water occurred at the addition of Fe₃O₄ by 120 mg with stirring time for 30 minutes. The adsorption efficiency of iron was 96.72%

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