SYNTHESIS AND CHARACTERIZATION OF SILICA GEL/CHITOSAN COMPOSITE DERIVED FROM TIN TAILING FOR REMOVAL OF Fe(III) IN POST-TIN MINING WATER

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Abstract

A study on the synthesis and characterization of silica gel/chitosan composite derived from tin tailings for removal of Fe(III) in post-tin mining water has been carried out. The silica source used for the synthesis of silica gel is tin tailings. It is produced by the sol-gel method. The characteristics of silica gel from tin tailings sand are white powder with a silica content of 73.58% after compositing with 30 mL and 45 mL chitosan solution, showing that the chitosan phase was successfully formed together with the silica phase. Functional group analysis showed the presence of typical chitosan functional groups ($-NH_2$) at 1629 cm^{-1} and 1635 cm^{-1} and typical silica functional groups (-Si-O-Si) at 1000 cm^{-1} to 1020 cm^{-1}. These functional groups appeared in addition to all variations of the chitosan solution. Morphological analysis shows that in the addition of 45 mL chitosan solution, the silica gel/chitosan composite has a morphology in the form of small round particles with uneven surfaces and more dominant pores. Adsorption study of silica gel/chitosan composite on Fe(III) in post-tin mining water showed 95.5% adsorption efficiency in the addition of 45 mL chitosan solution. The adsorption condition observed is the adsorption time as a fixed variable in this study which is for 17 hours.

***Keywords**: adsorption, chitosan, composite, silica gel, tin tailing*

Introduction

Bangka Belitung is the largest tin-producing province in Indonesia, contributing around 90% of the national tin production. Tin production in Bangka Belitung not only supports the national economy but also contributes significantly to the global economy. Along with tin production, there are negative impacts on the environment. The issue of post-tin mining land leaves a problem that has not been handled properly until now. A total of 12,607 former tin mining lands (kolong) are scattered in Bangka Belitung (BPDASHL, 2018). Post-tin mining lands contain heavy metal contamination, such as Pb, Cd, Mn, Zn, Fe, and Cr (Kurnia and Rohaendi, 2023).

Previous studies have developed several adsorbent materials to reduce heavy metal contamination in post-tin mine land. Some adsorbents include activated carbon (Marina *et al*., 2020), silica gel (Livia *et al*., 2020), porous metal oxidation (Kim *et al*., 2023), and CNT (Carvalheiras *et al*., 2023). Among these adsorbents, silica gel has characteristics such as being stable in an acidic atmosphere, having a large sorption capacity, being easy to produce, and being relatively inexpensive in organic solvents when compared to organic polymer resin solids. Research opportunities for silica

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gel are very large because the raw materials for silica gel can be found easily and abundantly, one of which is in the form of tin tailings sand, which is no longer utilized.

Silica gel is a form of silica produced by agglomerating sodium silicate sol (Na_2SiO_3) that can be utilized as an absorbent, desiccant, and catalyst precursor. Silica gel is known as one of the best coating materials for nanoparticles because it has good chemical stability, but silica gel also has several disadvantages, including the type of active groups in the form of silanol (Si-OH) and siloxane (Si-O-Si) groups that play a role in the adsorption process. This group causes limited selective adsorption capacity, weak mechanical properties, and limited regeneration ability (Pawitra, 2021). Silica adsorbents are less effective for adsorbing metals. This is because the oxygen atom in the silanol group has a low free electron pair donor ability. Therefore, modification of functional groups is needed to increase adsorption (Prehatini and Amaria A, 2023)

Modification of silica functional groups with chitosan can improve the adsorption of metal ions, mechanical properties, and selectivity. Chitosan has active amine ($-NH_2$) and hydroxyl (-OH) groups that can increase metal ion adsorption (Prehatini and Amaria A, 2023). Chitosan is influential because it has free amino groups ($-NH_2$) that can increase adsorption capacity, and chitosan hydroxyl can form hydrogen bonds. Amino groups and hydroxyl groups with high reactivity allow various chemical modifications that can be made to chitosan to increase adsorption to metals by adding silica (Riskadita, 2017). The uptake of chitosan in the absorption of iron metal is 93.27% (Rumapea, 2009). The combination of chitosan adsorbent with silica will produce high porosity and a large surface area. According to Nuha (2021), silica has an efficiency in adsorbing heavy metals of 84.99%. According to research by Pawitra *et al*. (2021), chitosan/silica adsorption can adsorb heavy metals by 99.3%. Based on previous research studies, silica gel/chitosan has the potential to be used as a heavy metal adsorbent material, therefore the novelty of this research is that there has been no research on the utilisation of tin tailings sand as a source of silica for silica gel/chitosan and no application of the adsorbent on post-tin mining water.

Research Methods

Materials

The materials used in this study are tin tailings sand, sodium hydroxide p.a (NaOH) (Merck, Germany), distilled water, hydrochloric acid p.a (HCl) (Merck, Germany), chitosan p.a (Sigma Aldrich, America), acetic acid p.a (CH_3COOH) 3% (Merck, Germany), iron sulfate heptahydrate p.a ($FeSO_4.7H_2O$) (Merck, Germany), sodium tripolyphosphate p.a ($Na_5P_3O_{10}$) 1% (Merck, Germany).

Instrumentation

The instrumentation in this research is X-ray diffraction (XRD) (ShimadzuXRD-7000), X-ray fluorescence (XRF) (Shimadzu 8201 PC), Fourier Transform Infra-Red (FTIR) (84000S), Scanning Electron Microscopy (Thermo Fisher Scientific, phenom P-series) and Atomic Absorption Spectrophotometer (AAS) (Perkin Elmst Analyst 100).

Procedure

The methods in this research include preparation of silica gel from tin tailings sand, synthesis of silica gel-chitosan composite, characterization of silica gel and silica-chitosan composite, and removal of Fe(III) in post-tin mining water.

1) Preparation of silica gel from tin tailings sand

   The tailings sand was weighed as much as 400 g, then washed with distilled water and stirred using a stirrer for 5 minutes. The washing process was repeated three times to remove soil and other impurities. The tailings sand was dried at 105 °C for 2 hours, then sieved with a 200 mesh sieve. Tailings sand powder was weighed 50 g and soaked in 200 mL of 2 M HCl for 12 hours. Next, the tailings sand was washed with distilled water until neutral. Then, the tailings sand was filtered and dried at 105 °C for 2 hours. The results were crushed, and then 16 grams of tailings sand powder was dissolved in 240 mL of 7 M NaOH solution and refluxed at 105 °C while stirring using a magnetic stirrer for 6 hours to form a mixture (sodium silicate).

Furthermore, the sodium silicate mixture was mixed with 240 mL of distilled water and allowed to stand for 24 hours then filtered. The filtrate was then titrated using 2 M HCl solution to pH seven until it was continuously stirred using a magnetic stirrer until a white precipitate formed. The white precipitate formed was then allowed to stand until room temperature and washed using hot distilled water five times. Then filtered and dried at 105 °C for 5 hours. The white powder obtained is the extracted silica gel (Naat *et al*., 2020).

2) Synthesis of silica gel-chitosan

Chitosan was prepared by dissolving 1 gram of chitosan into 100 mL of 3% acetic acid and stirring constantly using a magnetic stirrer for 1 hour until homogeneous. Furthermore, 1 gram of sodium tripolyphosphate powder was dissolved in 100 mL of distilled water and stirred constantly using a magnetic stirrer until homogeneous. The prepared silica was then mixed with chitosan solution with the addition of 15 mL, 30 mL, and 45 mL chitosan solution and stirred until homogeneous for 12 hours using a magnetic stirrer. The mixture was neutralized with 50 mL of 1M NaOH and allowed to stand until a precipitate formed. The resulting precipitate was decanted and washed with distilled water three times before being filtered. The resulting residue was reacted again with 30 mL of 3% acetic acid and mixed with 50 mL of 1% (b/v) sodium tripolyphosphate while stirring with a stirrer for 1 hour. The result obtained was filtered with filter paper, heated at 600 °C for 5 hours, then cooled in a desiccator. The results were crushed to get a homogenized size (Naat *et al*., 2020).

3) Characterization of silica gel and silica-chitosan composite

Characterization was carried out to determine the characteristics of silica gel and the resulting composite. The characteristics of silica gel are known from the analysis of silica composition using XRF analysis. Furthermore, the characteristics of the chitosan silica composite were carried out through crystal phase analysis using XRD, functional group analysis using FTIR, and morphological analysis using SEM.

4) Removal of Fe(III) in post-tin mining water.

Silica-chitosan was added to the water sample. The adsorbent and water mixture was stirred and allowed to stand for 17 hours. Then, it was filtered to separate the adsorbent with water. Each water was analyzed using an atomic absorption spectrometer (AAS) to determine the number of adsorbed ions. Furthermore, the adsorption efficiency of Fe(III) was determined using the formula are shown in the Equation (1) (Amelia *et al*., 2024).

$$\text{Adsorption efficiency (\%)} = \frac{\text{Co (initial concentration)-Ce (final concentration)}}{\text{Co (initial concentration)}} \times 100\% \quad (1)$$

Results and Discussion

Characterization of silica gel

The process of preparing silica from tin tailings sand is initiated by obtaining silica filtrate through an extraction process. Tin tailings sand is washed using distilled water to remove impurities and then crushed to a small size to facilitate contact with other compounds. Furthermore, the tailings sand is reacted with an HCl solution to remove contaminants and organic compounds attached to the silica surface, then neutralized with distilled water and dried to remove moisture content.

The prepared tailings sand was then hydrothermally extracted using NaOH precursor. The hydrothermal method is a method that can control size, increase crystallinity, and high homogeneity. The function of NaOH solution is to dissolve silica (SiO_2) contained in sand powder because silica is easily soluble in alkaline bases, especially strong bases such as hydroxy alkali. The reactions in Equation (2) occur during the extraction process.

$$SiO_{2(s)} + NaOH_{(aq)} \rightarrow Na_2SiO_{3(aq)} + H_2O_{(l)} \quad (2)$$

The sodium silicate obtained is then carried out through coprecipitation. At this stage, the resulting sodium silicate mixture is soaked with distilled water to optimize the dissolution of sodium silicate. After soaking, two layers are formed, namely the filtrate layer and the residue (insoluble part). Furthermore, the filtrate is reacted with HCl until a white precipitate is formed. This process is called the coprecipitation process. HCl reacts with sodium silicate (Na_2SiO_3) to produce silicic acid ($Si(OH)_4$). This silicic acid then undergoes polymerization and condensation, forming a three-dimensional structure known as silica gel.

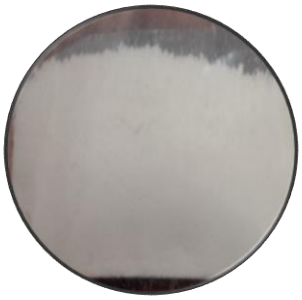


Figure 1. Silica gel

Based on Figure 1, physically, silica gel is a white powder. This is in accordance with the research of Landi Pote *et al*. (2023), which states that silica gel, in addition to HCl, produces white silica.

Table 1. Composition of silica gel

Oxide	Composition (%)
SiO_2	**73,583**
Al_2O_3	19,473
P_2O_5	4,651
CaO	1,471
Fe_2O_3	0,363

Based on Table 1, it is known that the composition of silica gel is dominated by silica at 73.58%, followed by other impurity compounds. These results are in accordance with the research of Fabiani *et al*. (2024), where silica sourced from tin tailings sand has other accompanying compounds such as Al_2O_3, P_2O_5, CaO, and Fe_2O_3.

Characteristics of silica-chitosan composites

Chitosan is prepared by dissolving chitosan with acetic acid. Chitosan is very soluble in acidic conditions because the carboxyl group of acetic acid facilitates the dissolution of chitosan in water due to hydrogen interactions between the carboxyl group of acetic acid and the amine group of chitosan. Chitosan dissolved in acetic acid occurs in a protonation reaction that produces an amine salt on the chitosan group, as in the following reaction (Equation (3)).

$$R\text{-}NH_2 + CH_3COOH \leftrightarrow R\text{-}NH_3^+\ CH_3COO^- \quad (3)$$

The interaction between chitosan and silica occurs due to the presence of NH_2^+ groups in the chitosan solution with OH from silica. The chitosan silica composite has active groups NH_2^+ and OH on chitosan, and Si-OH (silanol) and Si-O-Si (siloxane) on silica. These active groups may be able to interact with negatively charged metal ions. Furthermore, the silica-chitosan solution was neutralized with NaOH to form a solid gel. Furthermore, the solid gel is reacted with sodium tripolyphosphate as a thickening agent and cross-linking agent because it can be ionized to produce tripolyphosphate polyanions that can bind to chitosan polycations in acidic media. Tripolyphosphate polyanions bound to chitosan polycations will be able to add -OH and phosphate groups that can function as Lewis bases so as to increase the adsorption ability of silica-chitosan (Susilowati *et al*., 2018).

Characterization of silica-chitosan was carried out through several analyses. Analysis of the crystalline phase of silica chitosan was carried out through XRD analysis, as shown in Figure 2. Based on Figure 2, it is known that silica gel-chitosan was successfully formed with the presence of phases that appeared, namely silica and chitosan phases, in the addition of 30 mL and 45 mL chitosan. The silica phase is seen at 2θ = 44° and the chitosan phase at 2θ = 26°. This result is in accordance with the Silica ICDD database No. 01-085-0462 and Chitosan ICDD No. 00-039-1894.

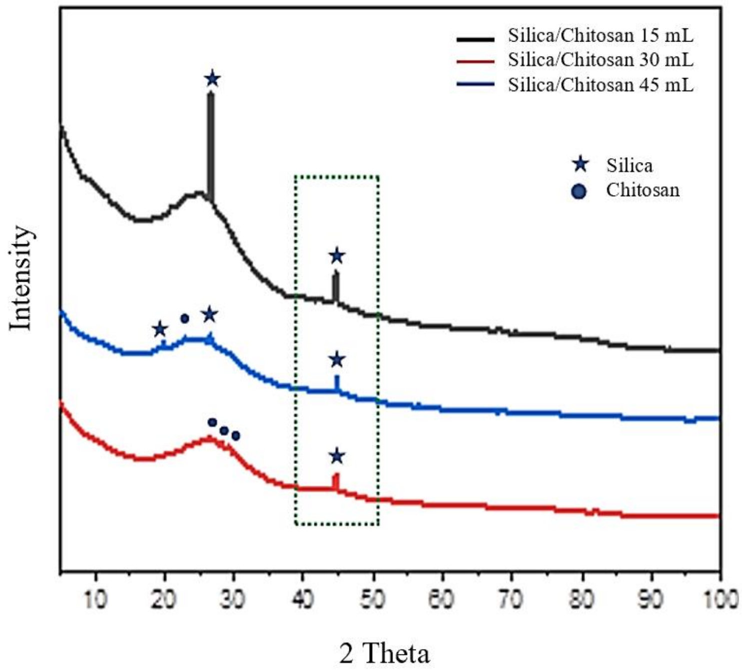


Figure 2. Diffractogram of silica-chitosan

Further characteristics were observed from the analysis of functional groups using FTIR. FTIR analysis was carried out to see the functional groups that appear on the silica-chitosan composite, as shown in Figure 3.

Figure 3 shows the presence of functional groups $-NH_2$, OH, Si-O-Si, and Si-OH. The absorption in the 3000–4000 cm^{-1} band is a typical peak for the stretching vibration of the -OH group (hydroxyl group). The hydroxyl groups on silica-chitosan come from the bonding of Si-OH groups (silanol groups), although the contribution of OH groups from water cannot be ignored. Absorption at wavelengths indicates the presence of amine groups (NH_2) on silica-chitosan derived from chitosan. Absorption at wavelengths of 1013 cm^{-1} and 1020 cm^{-1} indicates the presence of Si-O asymmetry stretching vibrations in Si-O-Si siloxanes. The Si-O-Si and Si-OH groups found in silica-chitosan come from silica. Si-O-Si and Si-OH groups are active groups of silica that form pores with silica-oxygen bonds between molecules so that long chains of SiO_2 and bonds between silica and oxygen in the -OH group are formed (Susilowati, Mahatmanti, and Haryani, 2018). The results of FTIR testing carried out on silica-chitosan show the presence of amine groups ($-NH_2$) at 1629 cm^{-1} and 1635 cm^{-1}, which occurs due to the addition of chitosan to silica.

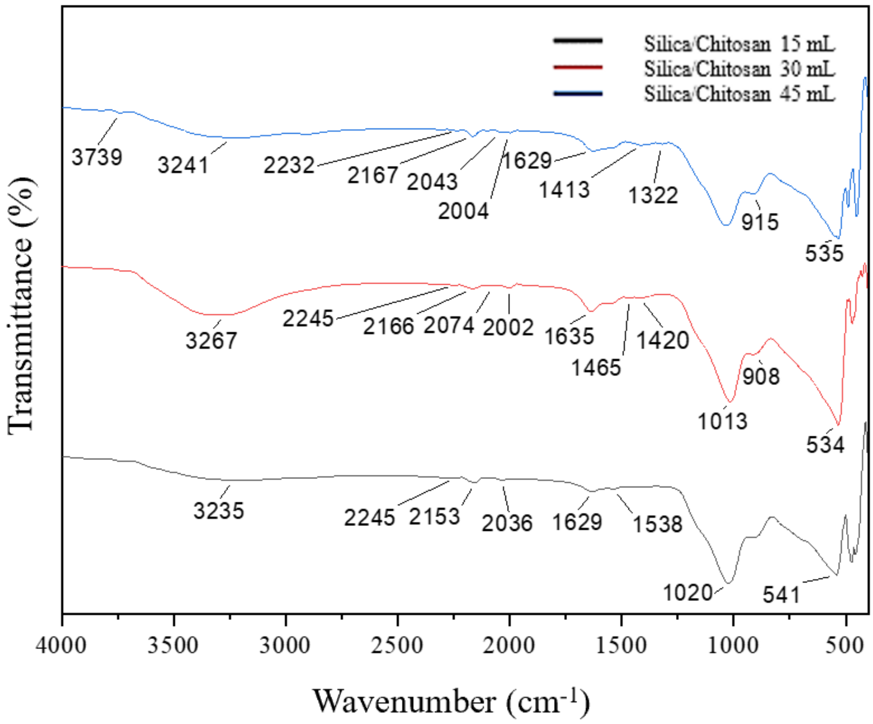
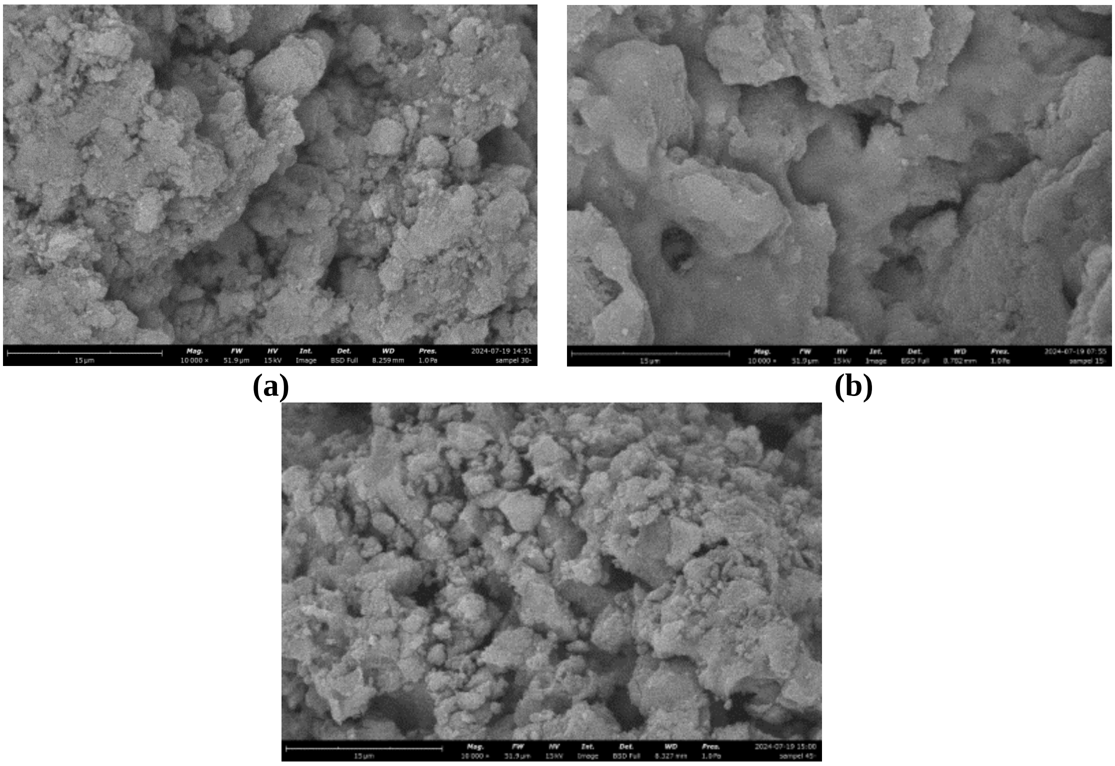


Figure 3. FTIR spectrum of silica-chitosan composite

Further characteristics were observed from morphological analysis using SEM, as shown in Figure 4. Based on Figure 4, it appears that the addition of chitosan causes the composite surface to be uneven. With the addition of 45 mL chitosan, the composite shows the presence of spherical particles. This is in accordance with the research of El-Barghouthi *et al.* (2008) where the silica-chitosan composite particles are spherical with an uneven surface. The uneven surface and non-uniform shape indicate that the added silica still contains many impurities and still dominates on the surface of the composite, the addition of chitosan does not have a significant effect on the resulting shape.



(a) (b) (c)

Figure 4. SEM analysis results of silica chitosan composites (a) 15 mL (b) 30 mL (c) 45 mL at 10,000× magnification.

Removal of Fe(III) in post-tin mining water

An adsorption study of heavy metals was conducted on Fe metal in tin mine water. Fe metal is the largest heavy metal in tin mine waters. The results of the AAS analysis are shown in Table 2.

Based on Table 2, it is obtained that the 45 mL Silica-Chitosan composite has the largest adsorption efficiency of 95.5%. The results of this adsorption efficiency are in line with the characterization data. Based on XRD data, silica/chitosan 45 mL shows that the composite was successfully formed due to the presence of silica and chitosan phases that appear on the diffractogram, this data is also supported by FTIR data where there are typical functional groups of chitosan and silica and SEM images where the morphology of silica/chitosan 45 mL shows many aggregated particles resembling a spherical shape.

Table 2. Adsorption efficiency results

Adsorbent	C initial (mg/L)	C final (mg/L)	C absorbed (mg/L)	Efficiency (%)
Silica-Chitosan 15	1.066	0.0896	0.9764	91.6%
Silica-Chitosan 30	1.066	0.2757	0.7903	74.13%
Silica-Chitosan 45	1.066	0.0475	1.0185	95.5%

Conclusions

Silica from tin tailings sand can be used as a source of silica for the synthesis of silica gel/chitosan composites so it can be a solution in utilizing unoptimized tin tailings sand. The characteristics of silica gel from tin tailings sand are white powder with a silica content of 73.58% after compositing with 30 mL and 45 mL chitosan solution, showing that the chitosan phase was successfully formed together with the silica phase. Functional group analysis showed the presence of typical chitosan functional groups (-NH_2) at 1629 cm^{-1} and 1635 cm^{-1} and typical silica functional groups (-Si-O-Si) at 1000-1020 cm^{-1}. These functional groups appeared in addition to all variations of the chitosan solution. Morphological analysis shows that in the addition of 45 mL chitosan solution, the silica gel/chitosan composite has a morphology in the form of small round particles with uneven surfaces and more dominant pores. Adsorption study of silica gel/chitosan composite on Fe (III) in post-tin mining water showed 95.5% adsorption efficiency in the addition of 45 mL chitosan solution. The next study is expected to consider adsorption conditions through various variations such as pH, time and adsorption concentration.

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