Preparation of Silica Adsorbent from Tin Tailing Sand by Alkali Fusion–Acid Leaching for Methylene Blue Removal

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ABSTRACT
The valorization of mining waste into functional materials provides a sustainable approach to environmental remediation and resource utilization. This study investigated silica recovered from tin tailing sand via an alkali fusion–acid leaching process as a low-cost adsorbent for methylene blue (MB) removal. Batch adsorption experiments were conducted using 50 mL of 10 mg/L MB solution with silica dosages ranging from 0 to 1.0 g. Residual MB concentration was determined by UV–Visible spectrophotometry at 664 nm, while turbidity measurements were performed to evaluate the effect of suspended silica particles. Adsorption performance strongly depended on adsorbent dosage, with the highest removal efficiency (98.32%) achieved at 0.2 g of silica. Increasing the dosage beyond this optimum did not improve MB removal, with efficiencies ranging from 90.55% to 97.78%, accompanied by a marked increase in turbidity. This behavior indicates that excessive silica loading promoted particle aggregation and suspended fine particles, reducing the accessibility of adsorption sites. These findings demonstrate that silica derived from tin tailing sand is an effective adsorbent for methylene blue removal and emphasize the importance of optimizing adsorbent dosage to maximize adsorption efficiency while minimizing suspended solids, supporting the sustainable utilization of tin mining waste for wastewater treatment.

ABSTRAK
Pemanfaatan limbah pertambangan menjadi material fungsional merupakan pendekatan berkelanjutan untuk mendukung pemanfaatan sumber daya dan pengendalian pencemaran lingkungan. Penelitian ini mengkaji pemanfaatan silika hasil ekstraksi pasir tailing timah melalui proses fusi alkali–pelindian asam sebagai adsorben berbiaya rendah untuk menghilangkan metilen biru (MB). Uji adsorpsi dilakukan menggunakan 50 mL larutan MB 10 mg/L dengan variasi dosis silika 0–1,0 g. Konsentrasi MB sisa dianalisis menggunakan spektrofotometer UV–Vis pada panjang gelombang 664 nm, sedangkan kekeruhan diukur untuk mengevaluasi pengaruh partikel silika tersuspensi. Kinerja adsorpsi sangat dipengaruhi oleh dosis adsorben, dengan efisiensi penyisihan tertinggi sebesar 98,32% pada dosis 0,2 g. Peningkatan dosis di atas kondisi optimum tidak meningkatkan penyisihan MB (90,55–97,78%) dan diikuti oleh peningkatan kekeruhan yang signifikan. Hasil ini menunjukkan bahwa penambahan silika berlebih menyebabkan agregasi partikel dan meningkatnya partikel halus tersuspensi sehingga mengurangi aksesibilitas situs adsorpsi. Temuan ini menegaskan bahwa silika dari tailing timah berpotensi sebagai adsorben efektif untuk pengolahan air limbah, dengan optimasi dosis menjadi faktor penting untuk memperoleh kinerja adsorpsi yang maksimal.

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KEYWORDS
Silica, Wastewater, Tin tailing

INTRODUCTION

The continuous discharge of dye-containing wastewater has become a major environmental concern due to the rapid expansion of textile, paper, leather, pharmaceutical, and printing industries. Synthetic dyes are designed to exhibit high chemical stability, resistance to light degradation, and long-term color durability, characteristics that also make them persistent contaminants once released into aquatic environments. Among various synthetic dyes, methylene blue (MB) is one of the most widely used cationic dyes because of its excellent solubility and color intensity. However, the persistence of MB in water bodies reduces light penetration, inhibits photosynthetic activity, disrupts aquatic ecosystems, and poses potential health risks including eye irritation, skin disorders, respiratory problems, and gastrointestinal toxicity when present at elevated concentrations (Crini & Lichtfouse, 2019; Salem et al., 2023). Consequently, the development of efficient and sustainable technologies for MB removal remains an important research topic in wastewater treatment.

Numerous technologies have been investigated for dye removal, including coagulation–flocculation, advanced oxidation processes, membrane filtration, photocatalysis, biological degradation, and adsorption. Although advanced oxidation and photocatalysis can achieve high degradation efficiencies, they generally require high energy input and expensive oxidizing agents. Membrane separation offers excellent effluent quality but suffers from membrane fouling and high operational costs, whereas coagulation generates large amounts of secondary sludge requiring further treatment. Compared with these techniques, adsorption has emerged as one of the most attractive approaches because of its simple operation, high removal efficiency, regenerability, and economic feasibility. Nevertheless, the overall performance of adsorption is strongly governed by the physicochemical properties of the adsorbent, highlighting the urgent need to develop inexpensive and sustainable adsorbent materials from abundant waste resources (Foo & Hameed, 2010; Crini et al., 2019).

Silica-based materials have attracted considerable attention as adsorbents owing to their excellent chemical stability, tunable porous structure, high specific surface area, and abundant surface silanol (Si–OH) groups that provide active adsorption sites. These characteristics enable silica to interact with organic pollutants through electrostatic attraction, hydrogen bonding, and surface complexation. Commercial silica, however, is commonly produced from high-purity quartz using energy-intensive and relatively costly processes, limiting its large-scale application in wastewater treatment. To reduce production costs while promoting resource sustainability, increasing attention has been directed toward extracting silica from industrial and agricultural wastes, including rice husk ash, fly ash, waste glass, and mining residues (Kalapathy et al., 2000; Awual, 2019).

Tin tailings are among the largest mining wastes generated worldwide. Indonesia, particularly the Bangka Belitung Islands Province, is among the world's major tin-producing regions, producing millions of tons of tailing sand annually. These tailings are generally stockpiled around mining areas, occupying large areas of land and creating long-term environmental challenges. Interestingly, tin tailing sand is predominantly composed of silica minerals, suggesting it could serve as an inexpensive alternative silica source rather than being treated solely as mining waste. Converting this underutilized waste into functional adsorbent materials is therefore consistent with the principles of the circular economy and sustainable resource utilization.

Various extraction routes have been proposed to recover silica from mining and industrial wastes, including acid leaching, alkali extraction, hydrothermal treatment, and alkali fusion. Among these methods, the combination of alkali fusion followed by acid leaching offers significant advantages because alkali fusion converts crystalline silica into soluble sodium silicate, facilitating subsequent purification and precipitation of high-purity amorphous silica. Despite these advantages, previous studies have primarily focused on maximizing silica recovery or improving silica purity, while comparatively little attention has been devoted to evaluating the adsorption performance of the recovered silica toward organic dye pollutants. Moreover, systematic investigations correlating extraction-derived silica characteristics with MB adsorption performance remain scarce, particularly for silica recovered from Indonesian tin tailing sand.

Therefore, this study aims to recover silica from Bangka tin tailing sand using an alkali fusion–acid leaching route and evaluate its potential as a low-cost adsorbent for MB removal from aqueous solution. The adsorption performance was subsequently investigated by varying the adsorbent dosage to elucidate its influence on MB removal efficiency. This work not only demonstrates a sustainable pathway for valorizing abundant mining waste into functional silica adsorbents but also contributes to the development of cost-effective wastewater treatment materials within a circular economy framework.

METHODS

Silica was extracted from tin tailing sand through an alkali fusion–acid leaching process. Prior to extraction, the tailing sand was thoroughly washed with distilled water to remove adhering impurities and dried in an oven until a constant weight was achieved. The dried sand was then mixed with sodium hydroxide (NaOH) pellets at a 1:1

mass ratio (tailing sand:NaOH) and homogenized before being transferred to an alumina crucible. The mixture was subjected to alkali fusion in a muffle furnace at 700°C to convert the silica minerals into soluble sodium silicate according to the reaction:

$$SiO_2+2NaOH \rightarrow Na_2SiO_3+H_2O$$

After cooling to room temperature, the fused product was dissolved in distilled water under continuous stirring, then filtered to remove insoluble residues. The resulting sodium silicate solution was subsequently neutralized by gradual addition of hydrochloric acid (HCl) until the solution reached pH 7, leading to the formation of silica gel through acid precipitation.

The silica gel was aged for 24 h at room temperature to promote the development of the gel network and improve structural stability. Subsequently, the gel was filtered and repeatedly washed with distilled water until chloride ions were completely removed, minimizing residual sodium chloride impurities. The purified gel was then dried to obtain silica powder. A schematic illustration of the extraction procedure is presented in Figure 1.

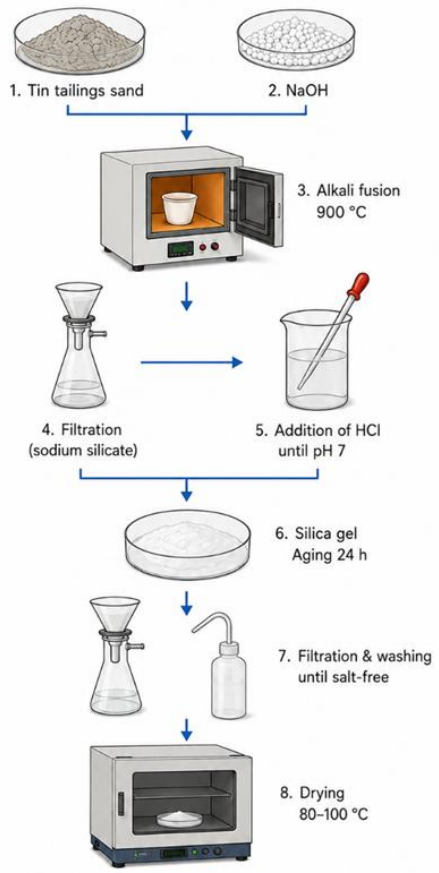


Figure 1. Silica synthesis scheme from tin tailings sand through alkaline fusion and acid leaching methods.

The adsorption performance of the synthesized silica was evaluated using MB as a model organic contaminant. A stock MB solution was prepared and diluted to obtain an initial concentration of 10 mg/L. For each adsorption experiment, 50 mL of MB solution was transferred into a beaker, followed by the addition of silica adsorbent with varying masses of 0, 0.2, 0.4, 0.6, 0.8, and 1.0 g. The suspension was stirred continuously with a magnetic stirrer for 60 min to ensure sufficient contact between the adsorbent and adsorbate.

After adsorption, the suspension was filtered to separate the silica particles from the solution. The residual MB concentration in the filtrate was determined using a UV–Visible spectrophotometer at the maximum absorption wavelength (λ_{max}) of MB. The residual dye concentration was calculated from a calibration curve prepared using standard MB solutions. The overall experimental procedure is illustrated in Figure 2.

The adsorption efficiency was calculated using Equation (1):

$$\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where η is the adsorption efficiency (%), C_0 is the initial MB concentration (mg/L), and C_t is the MB concentration after adsorption (mg/L). The adsorption performance was evaluated by comparing the removal efficiencies obtained at different adsorbent dosages to determine the optimum silica mass for MB removal.

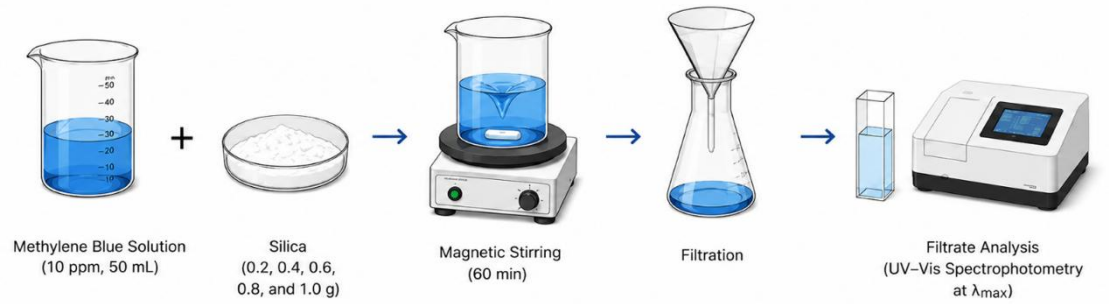


Figure 2. Methylene blue adsorption test scheme using synthesized silica.

RESULTS AND DISCUSSIONS

Prior to evaluating the adsorption performance, the UV–Visible absorption characteristics of MB were investigated to determine the optimum analytical wavelength and establish a reliable calibration curve for quantitative analysis. The absorption spectra of MB solutions with different concentrations are presented in Figure 3. All MB solutions exhibited a pronounced absorption peak at approximately 664 nm, corresponding to the characteristic electronic transition of monomeric MB molecules. Increasing the MB concentration from 0 to 10 mg/L resulted in a progressive increase in absorbance without any noticeable shift in the maximum absorption wavelength. The absence of spectral shifts indicates that no significant molecular aggregation occurred within the investigated concentration range, allowing the Beer–Lambert law to remain valid. The high linearity of absorbance at 644 nm demonstrates that absorbance is directly proportional to MB concentration throughout the studied range, confirming the suitability of the calibration curve for determining the residual dye concentration after adsorption.

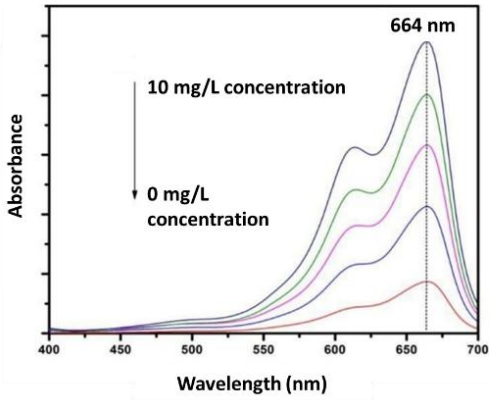


Figure 3. UV–Visible absorption spectra of methylene blue at different concentrations

The adsorption performance of the synthesized silica was initially evaluated through visual observation of the color change in the MB solution after treatment. As shown in Figure 4, the untreated solution displayed a deep blue color characteristic of the initial dye concentration. Upon addition of silica adsorbent, the blue coloration gradually faded as the adsorbent dosage increased.



Figure 4. Visual changes in the color of the methylene blue solution after the adsorption process using variations in silica mass.

To quantitatively evaluate the adsorption performance, the residual concentration of MB after adsorption was determined using UV–Visible spectroscopy at the maximum absorption wavelength of 664 nm. The residual dye concentration was calculated from the calibration curve presented in Figure 3, and the corresponding adsorption efficiencies are summarized in Figure 5.

As shown in Figure 5, the adsorption efficiency strongly depended on the amount of silica added to the solution. In the absence of silica, no MB removal was observed. The addition of 0.2 g of silica resulted in the highest adsorption efficiency of 98.32%, indicating that the synthesized silica possessed excellent adsorption capability toward MB. Increasing the adsorbent dosage to 0.4 g produced a comparable removal efficiency of 97.78%. However, further increases in silica dosage to 0.6, 0.8, and 1.0 g led to lower adsorption efficiencies of 90.55%, 92.29%, and 93.38%, respectively.

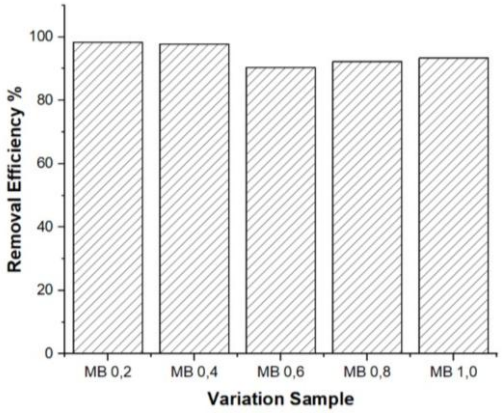


Figure 5. Changes in the absorbance of methylene blue solution after the adsorption process using variations in silica mass.

The exceptionally high removal efficiency achieved using only 0.2 g of silica indicates that the available adsorption sites were already sufficient to capture nearly all MB molecules present in the solution. Considering that the adsorption experiments employed 50 mL of a 10 mg/L MB solution, the total amount of dye available for adsorption was relatively small (approximately 0.5 mg). Consequently, increasing the adsorbent dosage beyond 0.2 g did not significantly increase the number of adsorbed dye molecules because the adsorption system had already approached equilibrium. Instead, excessive silica loading likely altered the physical behavior of the adsorbent particles rather than increasing the number of effective adsorption sites.

The adsorption of MB onto silica is primarily governed by electrostatic attraction between the positively charged MB molecules and negatively charged silanol (Si–OH) groups on the silica surface, together with hydrogen bonding and surface interactions. At low adsorbent dosage, these active sites remain highly accessible, allowing efficient interaction between dye molecules and the silica surface. In contrast, increasing the silica dosage increases the frequency of particle–particle collisions, promoting aggregation that may partially block accessible adsorption sites and reduce the effective surface area available for adsorption. Similar behavior has been reported for silica-based and other inorganic adsorbents, where excessive adsorbent loading decreases adsorption efficiency due to particle aggregation and reduced accessibility of active sites.

To further investigate the effect of silica dosage on the adsorption system, the turbidity of the filtrate after adsorption was measured, and the results are presented in Figure 6. The turbidity increased substantially with increasing silica dosage, from 7.32 NTU for the untreated MB solution to 26.2, 31.6, 73.4, 76.6, and 72.3 NTU after the addition of 0.2, 0.4, 0.6, 0.8, and 1.0 g of silica, respectively. Visual observation further confirmed that the filtrate obtained using 0.2 g of silica appeared clear, whereas progressively cloudier filtrates were observed at higher silica dosages. This trend indicates that increasing the amount of silica introduced a larger quantity of fine particles into the suspension, some of which were not completely retained during filtration using conventional filter paper.

Interestingly, the marked increase in turbidity coincided with the slight decrease in adsorption efficiency observed at silica dosages above 0.2 g. Although turbidity does not directly represent the residual MB concentration, the correlation between these two observations suggests that they originate from the same underlying phenomenon, namely changes in the dispersion behavior of silica particles. At higher adsorbent dosages, the increased particle concentration enhances interparticle collisions, promoting particle aggregation. Such aggregation can partially shield surface silanol groups and reduce the effective surface area available for MB adsorption. Simultaneously, the presence of very fine silica particles that remain suspended or pass through the filter paper contributes to the elevated turbidity values.

Therefore, the increase in turbidity should not be interpreted as evidence of poor dye removal but rather as an indicator of incomplete solid–liquid separation and altered particle dispersion at higher silica dosages. The UV–Visible measurements clearly demonstrate that MB removal remained above 90% for all silica dosages investigated, confirming that the synthesized silica maintained excellent adsorption performance despite the increased turbidity. These findings suggest that an adsorbent dosage of 0.2 g provides the best balance between adsorption efficiency and filtration performance, achieving nearly complete dye removal while minimizing suspended solids in the treated solution.

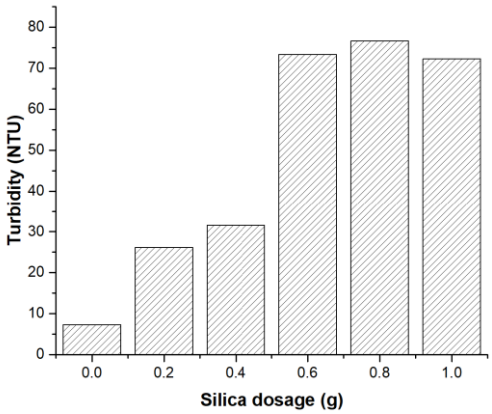


Figure 6. The relationship between silica dosage in the MB adsorption process and its turbidity

CONCLUSIONS

Silica recovered from tin tailing sand through the alkali fusion–acid leaching process exhibited excellent potential as a low-cost adsorbent for MB removal from aqueous solution. The adsorption performance was strongly influenced by the adsorbent dosage, with the highest removal efficiency of 98.32% achieved using 0.2 g of silica. Increasing the adsorbent dosage beyond this optimum level did not further improve dye removal and instead resulted in a slight decrease in adsorption efficiency.

The reduction in adsorption performance at higher silica dosages is likely associated with changes in particle dispersion behavior, including particle aggregation that decreases the accessibility of active adsorption sites. This interpretation is supported by the turbidity measurements, which showed a substantial increase in suspended silica particles as the adsorbent dosage increased. Therefore, excessive adsorbent loading may reduce the effectiveness of the adsorption process while simultaneously increasing the amount of residual suspended solids in the treated solution.

Overall, the results demonstrate that silica derived from tin tailing sand can serve as an efficient adsorbent for MB removal, providing a promising approach for transforming abundant mining waste into value-added materials for wastewater treatment. Further studies involving adsorption kinetics, equilibrium isotherms, adsorbent regeneration, and optimization of the solid–liquid separation process are recommended to support the practical application of this material in industrial wastewater treatment.

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