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Adsorption Behavior During Decolorization of Crude Glycerin Solution

Indok Nurul Hasyimah Mohd Amin* and Nursyakirah Ahmad Suhaimi

Section of Chemical Engineering Technology, Universiti Kuala Lumpur Malaysian Institute of Chemical & Bioengineering Technology, Lot 1988 Kaw. Perindustrian Bdr. Vendor, Taboh Naning, 78000 Alor Gajah, Melaka, Malaysia

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ABSTRACT

Crude glycerin, a by-product of the transesterification of oleochemicals, undergoes several processes to recover glycerine, which is commercially used in many daily personal care products. Crude glycerin is typically brown due to the solution's presence of lignin, tannin, and organic matter. This study uses sewage sludge as an adsorbent to decolorize crude glycerin through an adsorption process. Initially, the crude glycerin and the prepared adsorbent will be characterized using Fourier Transform Infrared Spectroscopy (FTIR) for functional groups, color concentration with UV-visible spectroscopy (UV-Vis), and particle size distribution using a Particle Size Analyzer (PSA). The adsorption behavior was elucidated at different agitation speeds (62.5 rpm, 125 rpm, and 250 rpm), adsorbent dosages (10 g/L, 20 g/L, and 30 g/L), and particle sizes of the adsorbent (100 microns, 200 microns, and 300 microns). The color intensity before and after adsorption was analyzed using UV-Vis spectroscopy, and the absorbance was used to determine the percentage of color removal. The findings showed that the optimum color removal from crude glycerin was achieved at 125 rpm agitation speed, 30 g/L adsorbent dosage, and 100 microns of adsorbent particle size, with 33.4%, 40.8%, and 40.2% of removal, respectively. At a 125 rpm agitation speed, the Langmuir isotherm fit the experimental data with K_L and q_{max} values of 0.0028 L/mg and 8.25 mg/g, respectively. The Freundlich isotherm could describe the adsorption process at 30 g/L adsorbent dosage with K_F and 1/n values of 0.142 mg/g and 0.135, respectively. Additionally, the experimental findings using 100 microns of adsorbent fit well with the Langmuir isotherm, with K_L and q_{max} values of 0.057 L/mg and 0.246 mg/g, respectively.

INTRODUCTION

Crude glycerin can be produced as a by-product from the transesterification of various sources within the biodiesel, soap, fatty ester, and fatty acid industries. About 1 kg of crude glycerin is produced for every 10 kg of biodiesel production due to the transesterification process [1]. The overproduction of crude glycerin and its low economic value due to contaminants complicating the purification process poses significant challenges. Contaminants such as methanol, salt, soap, triglycerides, fatty acids, and metals are

* Corresponding author. *E-mail address*: nurulhasyimah@unikl.edu.my
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formed due to the transesterification process. However, the specific contaminants present in crude glycerin may vary depending on the source [2]. Despite these contaminants, crude glycerin often appears as a dark brownish liquid, making color treatment an important step in clarifying crude glycerin to meet the US Pharmacopeia standard requirement.

Processes for clarifying crude glycerin in the oleo industry include acidification, distillation, ion exchange resin, membrane separation technology, neutralization, and solvent extraction. Acidification is used to purify crude glycerin by neutralizing the catalyst and other contaminants into inorganic salt [3], and converting soap to insoluble free fatty acid to avoid yield loss due to poor separation [4]. However, acidification cannot eliminate all impurities, such as water, methanol, oil, and ester in crude glycerin, necessitating further purification. Distillation, while a common purification method, has several disadvantages, including the need for high energy input and the risk of thermal decomposition. Moreover, distillation requires a high vacuum to prevent the denaturation of glycerin at high temperatures [5], leading to high maintenance costs and capital investment.

Decolorization is the removal of color from a solution and can be carried out through adsorption using sewage sludge as the adsorbent. This study chose sewage sludge over activated carbon for industrial applications due to the high cost associated with activated carbon, produced from the bottom product of petroleum refinery processes. As this source is non-renewable, activated carbon is bound to be depleted. Sewage sludge has been proven to remove unwanted impurities effectively, as demonstrated in research, such as the study by Hunsom & Autthanit, which utilized sewage sludge activated with different chemicals to purify crude glycerin [6].

The generation of sewage sludge has increased significantly due to population growth, urbanization, and industrialization. It was reported that the production of sewage sludge by Indah Water Konsortium for 2020 is expected to be 7 million m^3 [7]. With the overproduction of sewage sludge, most of it is disposed of in landfills, leading to environmental pollution [8]. Various studies have been conducted to explore the capability of sewage sludge as an adsorbent. Recently, Chenyu et al. [9] enhanced the adsorption performance of sewage sludge (SS) adsorbent for tetracycline and methylene blue through hydrothermal carbonization, finding that adsorption capacities increased by 16 and 101% compared to the blank sample. Another study reported that SS, rich in oxygen and nitrogen functional groups, could form hydrogen bonds with other precursors, significantly enhancing its adsorption capacity and making it an excellent adsorbent [10]. Thanks to its low cost and minimal environmental impact, attention has shifted towards deriving sludge-based activated carbon [11].

Studies on sewage sludge carbonization conducted at temperatures of 900°C for 70 minutes and 950°C for 30 minutes resulted in surface areas of 359 m^2/g and 141 m^2/g, respectively [12-13]. The variation in surface area may be attributed to differences in the drying process before carbonization or the organic content of the sewage sludge, which varied due to different sources. After carbonization, the ash content can be predicted from the surface area of the adsorbent, with a higher surface area typically resulting in lower ash content. Ash content serves as an indicator of inorganic content, as it comprises non-combustible material [14]. Therefore, this study focuses on adsorption performance under varying parameters such as agitation speed, adsorbent dosage, and particle size of the adsorbent to decolorize crude glycerin.

EXPERIMENTAL

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Preparation of adsorbent

The sewage sludge, a residue from the wastewater treatment plant (WWTP) of Indah Water Konsortium (IWK) located in the Klang Valley, is solid. Initially, the sludge was dried for 24 hours to remove moisture content. To activate sewage sludge, 10% zinc chloride ($ZnCl_2$) was mixed with the sludge. Then, the mixture was left to rest for 24 hours. The sludge underwent pyrolysis for 1 hour in a furnace to enhance its adsorption capacity. Subsequently, the sewage sludge was rinsed with 0.2 M hydrochloric acid (HCl) to remove excess activating agents and inorganic matter. Finally, distilled water was used to rinse the sludge, removing any remaining HCl. The activated sewage sludge was kept in a hot air oven to preserve its characteristics.

Characterization of adsorbent

The prepared adsorbent was characterized based on its functional group (FTIR) and particle size distribution (PSA).

Adsorption study

The crude glycerin was placed inside a beaker for adsorption. The activated sewage sludge adsorbent was added into the beaker and left for 90 minutes to allow adsorption. After that, the solution was filtered using a filter pump to recover the adsorbent for further analysis. The percentage of color removal identifies the optimum parameter for sewage sludge adsorbent to decolorize crude glycerin and was calculated based on Equation 1.

$$Decolorization\ efficiency = \frac{C_O - C_F}{C_O} \times 100\% \quad (1)$$

Where C_o is the initial concentration of crude glycerin, and C_F is the final concentration.

RESULTS AND DISCUSSION

Characterization of prepared adsorbent

Fig. 1 showcases the functional groups of the adsorbent, revealing that the adsorbent comprises both organic and inorganic compounds. The organic compounds in sewage sludge include fats, oil, carbohydrates, proteins, grease, and surfactants, while its inorganic components consist of nitrogen, chlorides, sulfur, and phosphorus. Three functional groups displayed prominent peaks. Firstly, the O-H group was represented by a peak at 3330.51 cm^{-1}, indicating that the hydroxyl group plays a critical role in impurity or solute uptake by enhancing chemisorption and fostering interaction between the solute and hydroxyl group [9,11]. Additionally, C-C vibrations in the aromatic ring were attributed to a peak at 1631.57 cm^{-1} [15] in the sewage sludge adsorbent. Lastly, the C-O of alcohol was detected at a peak of 1001.44 cm^{-1} [16].

Fig. 2 shows the particle size distribution of the sewage sludge adsorbent. The largest particle size distribution was noted at 15.136 microns, accounting for 4.69% of the distribution. The specific surface area was measured at 0.757 m^2/g, lower than activated carbon at 909 m^2/g [17]. This discrepancy can be attributed to the specific surface area of the adsorbent being dependent on the chemical activation and pyrolysis temperature [16]. In this study, $ZnCl_2$ was utilized for chemical activation, and the sewage sludge was pyrolyzed at 550°C, potentially affecting the efficacy of decolorization using sewage sludge adsorbent compared to commercial activated carbon.

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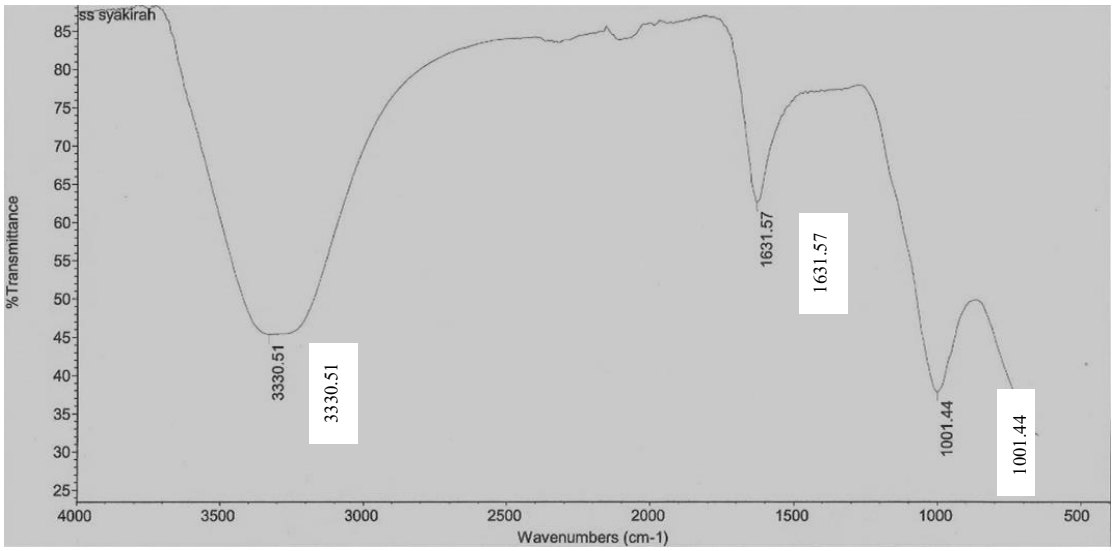

Fig. 1. The particle size distribution of the sewage sludge adsorbent.

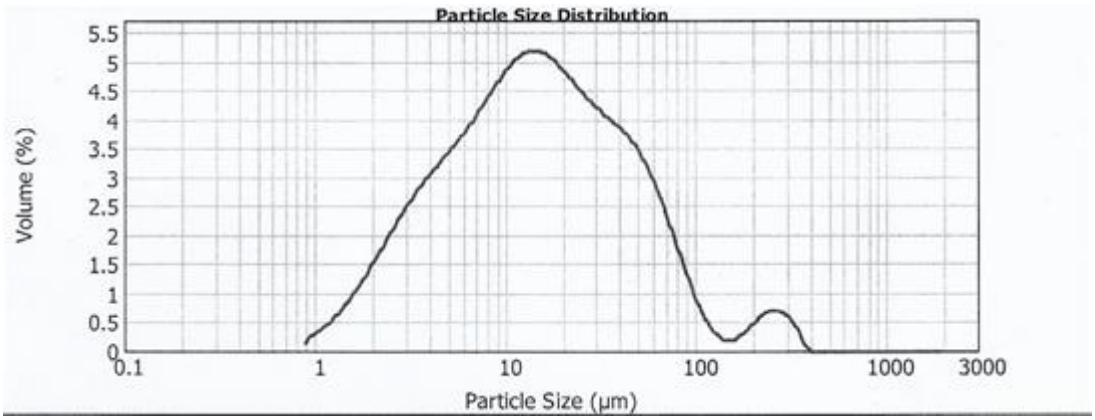

Fig. 2. Particle size distribution of adsorbent

Effect of agitation speed

Fig. 3 displays the adsorption behavior at different agitation speeds. The highest color removal was observed at a medium speed (125 rpm) with 33.4% removal, while the lowest was at the lowest speed (62.5 rpm) with 27.5% removal. This suggests that the adsorption rate increases with speed due to the induced turbulence effect, which helps to spread the adsorbate evenly and reduce the thickness of the boundary layer on the adsorbent surface [18]. Furthermore, the adsorbent may precipitate without sufficient agitation, disrupting the contact between the adsorbent and adsorbate [19]. At the highest speed (250 rpm), the percentage of removal was lower compared to 125 rpm and 62.5 rpm, possibly because fast stirring caused the adsorbent and adsorbate to be released prematurely.

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Additionally, it was noted that, for the first 20 minutes, color removal significantly increased for all speeds, likely due to the unsaturated condition at the available pore sites of the adsorbent, which increased the uptake of the adsorbate. However, after 40 minutes, the removal trend differed insignificantly as the available sites began to saturate and become occupied.

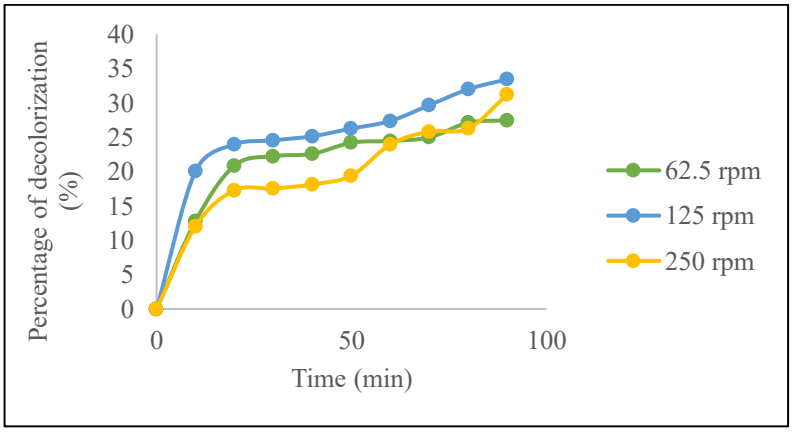
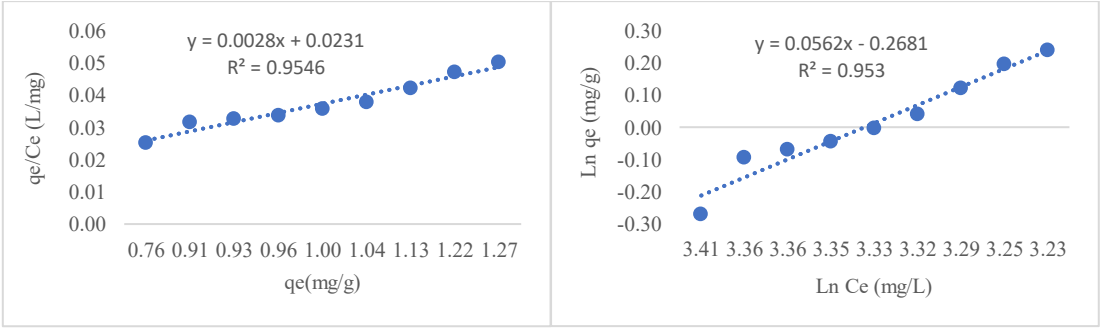


Fig. 3. Effect of agitation speed

Figures 4(a) and 5(b) illustrate the fitting of the adsorption data with Langmuir and Freundlich isotherms, respectively, showing that both isotherms fit the experimental data well with fitting coefficients greater than 0.950. The RL of the Langmuir isotherm's separation factor was 0.9038, indicating that the adsorption process for decolorizing crude glycerin was favorable. The Langmuir constant, K_L, obtained from the gradient of the graph, was equivalent to 0.0028 L/mg, while the maximum adsorption capacity, q_{max}, was equal to 8.25 mg/g.



(a) (b)

Fig. 4. (a) Langmuir isotherm and (b) Freundlich isotherm analysis (speed = 125 rpm)

Effect of adsorbent dosage

The adsorption behavior at various dosages (10, 20, and 30 g/L) is depicted in Fig. 5. Initially, there was a rapid increase in adsorption with an increase in adsorbent dosage. This suggests that as the adsorbent dosage increases, the amount of color adsorbed also rises due to the greater number of available

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adsorption sites resulting from the higher adsorbent dose, thereby increasing the amount of color adsorbed [20]. Notably, at 30 g/L, there was a spike in adsorption from minute 70 to minute 90, whereas the percentage change was not significant at 10 and 20 g/L dosages. This phenomenon could be attributed to the difference in active adsorption sites available simultaneously but with different adsorbent dosages [21]. The aggregation of color particles likely occurred under these conditions, reducing the available adsorbent sites due to pore coverage and, consequently, decreasing both the color uptake and the removal efficiency.

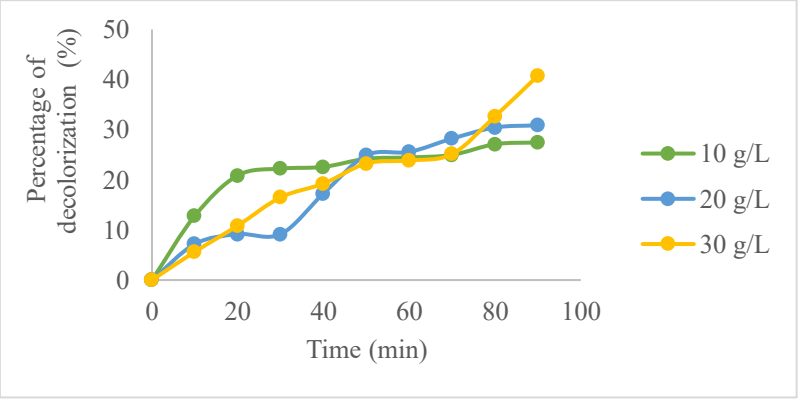
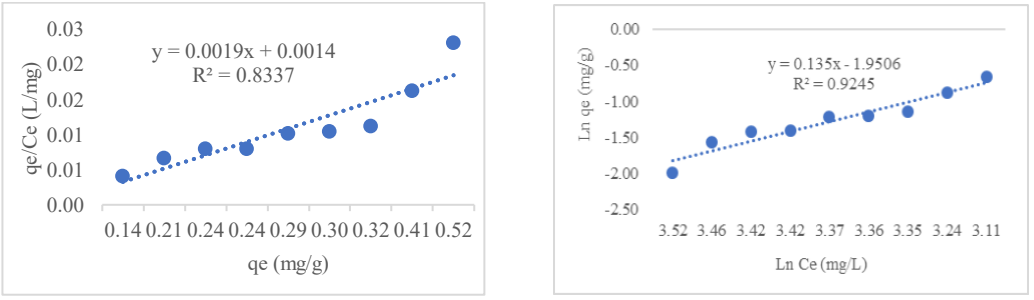


Fig. 5. Effect of adsorbent dosage

Figures 6(a) and (b) present the Langmuir and Freundlich isotherms' analysis for decolorizing crude glycerin with a 30 g/L adsorbent dosage. The Freundlich isotherm provided the best fit, with an R^2 value of 0.945. The analysis also revealed that the constant K_F was equivalent to 0.142 L/g, and the empirical constant, 1/n, interpreted as the y-intercept value, was equal to 0.135. With the value of 1/n ranging from 0.1 to 1, the adsorption process is considered favorable [19].



(a) (b)

Fig. 6. (a) Langmuir isotherm and (b) Freundlich isotherm analysis (dosage = 30 g/L)

Effect of adsorbent particle size

Fig. 7 illustrates the adsorption behavior during the decolorization of crude glycerin with different adsorbent particle sizes ranging from 100 to 300 microns. In the initial 10 minutes, it is evident that the smallest particle size (100 microns) achieved greater removal efficiency than the larger size (300 microns). This phenomenon can be attributed to smaller adsorbent particles offering a larger surface area and more adsorption sites [22]. Another study supports this observation, suggesting that smaller particle sizes lead to

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greater adsorption capacity, possibly because solutes prefer to adsorb on the surface of the adsorbent rather than penetrating its pores [23]. However, between minutes 30 and 50, the larger adsorbent particles (300 microns) surpassed the smaller ones in the percentage of removal. This could be due to a consequent change in the void fraction when altering the adsorbent particle size [24].

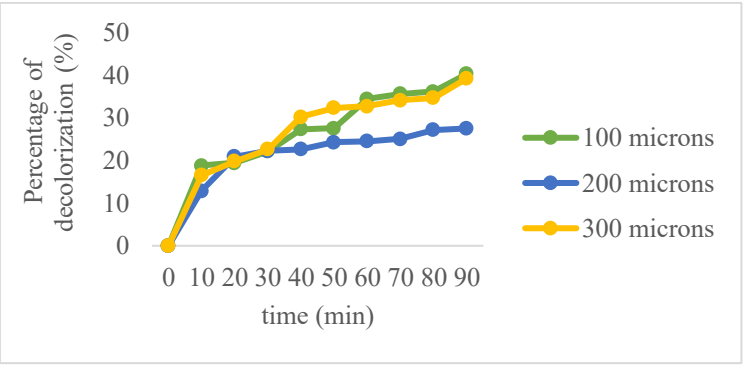
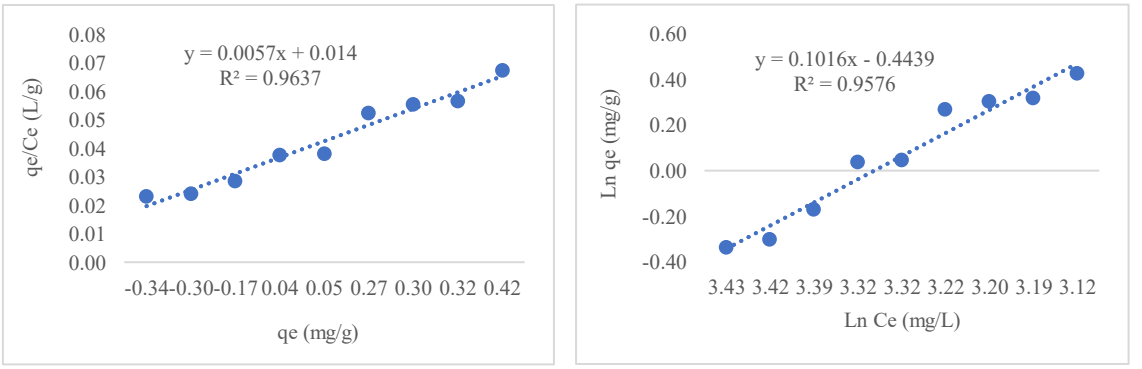


Fig. 7. Effect of adsorbent particle size

The fitting of the adsorption data was analyzed in Figures 8(a) and (b), demonstrating that both isotherms provide a good fit for the experimental data. The maximum adsorption capacity, q_{max}, was determined to be 0.246 mg/g, and the constant was 0.057 L/g. Furthermore, the value of the separation factor, R_L, was within the favorable range of 0 to 1, specifically at 0.316, indicating that the adsorption process is favorable.



(a) (b)

Fig. 8. (a) Langmuir isotherm and (b) Freundlich isotherm analysis (particle size = 100 microns)

CONCLUSION

To conclude, an agitation speed of 125 rpm resulted in 33.4% color removal from crude glycerin, whereas the lowest removal, at 27.5%, was observed with an agitation speed of 62.5 rpm. The variance in decolorization percentage is attributed to eliminating the boundary layer on the adsorbent due to turbulence at 125 rpm. At an agitation speed of 62.5 rpm, the adsorbent precipitated, disrupting the adsorption process and resulting in a lower decolorization percentage. Additionally, increased decolorization was observed with higher adsorbent dosages due to the augmentation of active adsorbent sites. An adsorbent particle size of 100 microns achieved the highest color removal at 40.2%, compared to 200 and 300 microns,

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demonstrating that a reduction in particle size leads to an increase in surface area where adsorption can occur. Furthermore, isotherm analysis revealed that both isotherms fit well with the adsorption behavior as agitation speed and adsorbent size varied, indicating the possibility of multilayer deposition of solute on the outer surface of the adsorbent. However, the Langmuir isotherm provided the best fit at different dosages, suggesting a monolayer deposition of solute on the adsorbent.

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AUTHOR'S CONTRIBUTION

Nursyakirah carried out the research and wrote and revised the article. Nurul Hasyimah designed the research, supervised the research progress, revised the article, and approved the submission.

CONFLICT OF INTEREST STATEMENT

The authors agree that this research was conducted without any self-benefits or commercial or financial conflicts and declare the absence of conflicting interests with the funders.

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