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Cationic Dye Adsorption Using Silica Xerogel from Corn Husk in A Continuous Fixed-Bed Column

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ABSTRACT. Silica xerogel from corn husks shows potential to be applied as an adsorbent for cationic dye removal due to its high adsorption capacity. However, the study regarding its performance in a continuous operation is still very limited, which hinders its application as a commercial adsorbent. To answer that problem, we investigate the adsorption of methylene blue (MB) and crystal violet (CV) dye using silica xerogel from corn husk in a continuous fixed-bed column. A breakthrough curve analysis was carried out with flow rate and bed height variations in an up-flow mode. The column effluent concentration was analyzed using a UV-Vis Spectrophotometer. The experimental data shows good agreement with the Thomas/Bohart-Adams and Yoon-Nelson model at different flow rates but has less correspondence for increasing bed height. Maximum adsorption capacities for methylene blue were 1.977 mg/g (Thomas/BA) and 1.743 mg/g (experimental). While for crystal violet the maximum adsorption capacities were 3.400 mg/g (Thomas/BA) and 4.573 mg/g (experimental).

Keywords: adsorption, cationic dyes, silica xerogel, fixed-bed column, mathematical model.

INTRODUCTION

In 2019, the Indonesian textile industry experienced growth of up to 15.08%. In addition, based on data from the Central Statistics Agency, in 2021 the export growth of the textile industry was 19.59% and valued as high as US$ 7.6 million (Riyardi et al., 2015). This significant increase contributed to not only the developing economy but also, negatively, to the high volume of wastewater being discharged into the environment. Textile wastewater contains a high amount of chemicals, especially dyes that are harmful to the surrounding environment. In aquatic ecosystems, the dyes can inhibit sunlight penetration which hinders the photosynthesis of aquatic plants, thus causing a lack of dissolved oxygen content (Baunsele & Missa, 2020).

The most common dyes in textile industries are crystal violet (CV) [$C_{25}H_{30}N_3Cl$] and methylene blue (MB) [$C_{16}H_{18}N_3SCl$]. CV and MB can survive in the environment for a long time due to their complex chemical structure, are resistant to decomposition by chemical, physical, and biological treatments, and have a toxic effect on aquatic life (Au et al., 1978). CV and MB can also negatively impact human health and are considered carcinogenic. Exposure to CV and MB can cause skin irritation, fever, vomiting, and gastrointestinal pain (Gürses et al., 2014).

Several methods have been used to remove those dyes, such as adsorption, photodegradation, biodegradation, enzymatic processes, coagulation, electrochemistry, and membrane filtration (Chen et al., 2012; Santoso et al., 2020; Wijaya et al., 2018). Compared to other methods, adsorption is one of the most preferable due to its high efficiency, relatively simple setup, and low cost. The adsorption process in general is also not sensitive to toxic substances and environmentally friendly (Kuang et al., 2020; Rafatullah et al., 2010).

Previous research has investigated the ability of silica xerogel as an adsorbent for cationic dye removal due to its high surface area and adjustable pore diameter. The maximum adsorption capacity of MB using silica xerogel from bagasse ash and volcanic tuff is 10.53 mg/g and 51.967 mg/g, respectively (Guzel Kaya et al., 2019; Maknun et al., 2018). On the other hand, silica xerogel from bagasse ash can adsorb CV with a maximum capacity of 26.53 mg/g (Naseem et al., 2021). In our previous research, CV and MB batch adsorption have been carried out using silica xerogel synthesized from corn husk via the sol-gel method. The as-obtained silica xerogel has an average pore diameter of 6.35 nm and a Brunauer, Emmett, and Teller (BET) surface area of 363.72 m^2/g. The particles are in irregular shapes, with sizes ranging from 80 to 250 µm, and have an atomic composition of 35.11% Si and 64.89% O. The maximum adsorption capacity was quite high, 69.44 mg/g for CV and 59.17 mg/g for (Dahliyanti et al., 2022). This result shows the potential of silica xerogel to be applied as an adsorbent in large-scale cationic dye removal.

However, all previous studies had been conducted only in batch mode. For a large-scale application,

continuous mode is preferred due to its high processing capacity. Fixed-bed column is the most common technique for industrial-scale adsorption processes (Xu et al., 2013). A breakthrough curve is used to represent the performance of a fixed-bed column by plotting the effluent and influent (C_t/C_0) concentrations as a function of time. A breakthrough occurs when the adsorbate concentration is first detected at the outlet (C_t) (Achazhiyath Edathil et al., 2020; Jiang et al., 2020; Patel & Vashi, 2015). The design and performance of a fixed-bed column are influenced by various parameters such as bed height, flow rate, inlet concentration, flow rate, flow direction, pH, temperature, as well as the interaction between adsorbate and adsorbent (Brion-Roby et al., 2018; Unuabonah et al., 2019).

Mathematical modeling is used in describing and predicting the dynamic behavior of fixed-bed adsorption in continuous operation. Several mathematical models are commonly used, including the Thomas, Yoon-Nelson, Adams-Bohart, and Bed Depth Service Time (BDST) models. These mathematical models have different calculation assumptions in determining their kinetic parameters.
Here, we study the dynamic behavior of methylene blue and crystal violet adsorption by silica xerogel from corn husk in a continuous fixed-bed column. The effect of flow rate and bed height on the adsorption performance of the column is investigated. The rate coefficient and kinetic parameters will be calculated by fitting the experimental data with the Thomas/Bohart-Adams and Yoon Nelson model. From this research, we hope to provide a basis for the design of cationic dye removal by adsorption on an industrial scale.

EXPERIMENTAL SECTION

Materials

Dry corn husk waste (local farmers), HCl 37% (Lab guard), crystal violet (Merck), methylene blue (Merck), NaOH pellets for analysis (Merck), silica xerogel GF254 for comparison (Merck), and demineralized water are used without any further purification.

Methods

Synthesis of Silica Xerogel

Silica xerogel was synthesized using the same sol-gel method as in our previous research (Dahliyanti et al., 2022). The dried corn husk waste was cut and then ground with a blender. Then, the corn husk powder was put into the furnace at 600°C for 2 h with a temperature ramp rate of 10°C per min to obtain the ash. Silica xerogel was synthesized from the ash by the sol-gel method. 0.25 g of corn husk ash was mixed with 6 mL of NaOH 1 M and then stirred at 80°C form sodium silicate (Na_2SiO_3). After 1 h, the Na_2SiO_3 solution was cooled down to room temperature and then centrifuged at 12,000 rpm for 10 minutes to separate the solid residue. The filtrate was titrated with HCl 3 M until it reached pH = 7. The solution was aged for 18 h at room temperature to promote the formation of a hydrogel. The resulting hydrogel was then washed repeatedly using demineralized water before being dried in an oven for 5 hours at 60°C to produce silica xerogel.

Characterization of Silica Xerogel

The functional groups of the as-obtained silica xerogel were identified using Thermo Fisher Scientific iS 5 Fourier Transform Infrared (FTIR) at λ = 4000 - 600 cm^{-1} with a sample and KBr ratio of 1:9. Crystallinity of the sample was examined using Olympus BTX-534 X-ray Diffraction (XRD) with Co-Kα radiation of 40 kV in the range $2\theta = 0 - 55^{\circ}$ and then converted to Cu-Kα.

Adsorption Experiment

A fixed-bed column was constructed with a height of 15 cm and an inner diameter of 0.9 cm. The glass wool was used to hold the silica xerogel adsorbent inside the column. The adsorbent bed height were 1 cm (0.30375 g), 3 (0.91 g) and 5 cm (1.5 g) cm. An initial concentration (C_0) of 10 mg/L dyes was pumped into the column in an up-flow direction with flow rates of 17, 26, and 29 mL/min. Adsorption was carried out at room temperature (25 °C) and a pressure of 1 atm. Samples were taken at the column outlet every 60 seconds and then analyzed using the Thermo Scientific GENESYS 10S UV-Vis Spectrophotometer with a maximum absorption wavelength for methylene blue of 664 nm and crystal violet of 590 nm. To obtain the effluent concentration from the absorbance data, a calibration curve must first be constructed. First, the absorbance of CV and MB solutions at various known concentrations was measured. Then, the concentration of the solutions (x-axis) and absorbance (y-axis) were plotted to obtain a linear equation:

$$y = bx + a \quad (1)$$

Where y is the absorbance, b is the slope of the calibration curve, x is the dye concentration in solution (mg/L), and a is the intercept.
The concentration of effluent at a given time (C_t) can be calculated using the equation below:

$$C_t = \frac{(y-a)}{b} \quad (2)$$

Pressure drops along the column were measured using a manometer. The column schematic is shown in **Figure 1**.

Column Data Analysis

Breakthrough curves were obtained by plotting the outlet to inlet concentration (C_t/C_0) versus adsorption time (t). The following equation is used to calculate the total amount of adsorbed dye (q_{total}) in the column for a given flow rate and feed concentration (Gong et al., 2015):

$$q_{total} = \frac{QA}{1000} \quad (3)$$

$$q_{total} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} C_{ad}\, dt \quad (4)$$

$$q_{total} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} (C_0 - C_t)\, dt \quad (5)$$

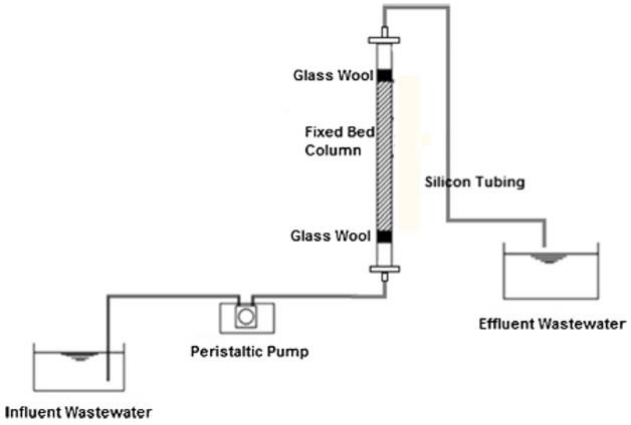

Figure 1. Adsorption column schematic.

Where q_{total} is the amount of adsorbed adsorbate (mg), t_{total} is the total adsorption time (min), Q is the fluid flow rate (mL/min.), A is the area under the curve (m^2), and C_{ad} is the concentration of adsorbed adsorbate (mg/L). The dye maximum adsorption capacity on silica xerogel was determined using the following equation:

$$q_e = \frac{q_{total}}{m} \quad (6)$$

m is the mass of adsorbent. The amount of adsorbate flowing into the column (m_{total}) is determined as:

$$m_{total} = \frac{C_0.Q.t_{total}}{1000} \quad (7)$$

Based on the calculation of the above equation, the % removal of dyes in the adsorption process can be calculated as:

$$\%removal = \frac{q_{total}}{m_{total}} \text{ x } 100\% \quad (8)$$

The Thomas model which is commonly used here and in other literature is actually another form of the Bohart-Adams model (Chu, 2010). However due to familiarity reasons, here we will call it as Thomas/BA model. The values of Thomas/BA model parameters, k_{TH} and q_0, are calculated from the slope and intercept of $\ln\left(\frac{C_0}{C_t}-1\right)$ versus time (t) plot based on the following equation (Biswas & Mishra, 2015; Brion-Roby et al., 2018; Saraf & Vaidya, 2018):

$$\ln\left(\frac{C_0}{C_t}-1\right) = \frac{k_{TH}.q_0.w}{Q} - k_{TH}.C_0.t \quad (9)$$

k_{TH} is the Thomas/BA rate constant (L/mg.min.) and q_0 is the maximum adsorption capacity (mg/g).

For the Yoon-Nelson model, the parameters k_{YN} and τ, are calculated from the slope and intercept of $\ln\left(\frac{C_t}{C_0-C_t}\right)$ versus time (t) plot which refers to the following equation (Brion-Roby et al., 2018).

$$\ln\left(\frac{C_t}{C_0-C_t}\right) = k_{YN.}(t-\tau) \quad (10)$$

Where k_{YN} is the Yoon-Nelson rate constant (min^{-1}), and τ is the time required to reach a 50% breakthrough (min.).

The mathematical model's fit is reviewed through the linear coefficient of determination (R^2) value. If the value of R^2 is close to one ($R^2 \sim 1$), it indicates that the adsorption process follows the mathematical model (Patel, 2019).

RESULTS AND DISCUSSION

Adsorbent Characterization

FTIR spectra of the as-synthesized silica xerogel from corn husk and commercial silica xerogel are shown in **Figure 2**. Silanol functional group peaks which were associated with Si-OH symmetrical bending and asymmetric stretching vibrations are identified at 1630 cm^{-1} and 3450 cm^{-1}. Meanwhile, peaks at 1100 and 800 cm^{-1} correspond to the stretching vibrations in Si-O-Si bonds (Silverstein et al. 2005). It can be concluded that the as-synthesized silica xerogel possesses similar functional groups as the commercial silica xerogel.

XRD patterns of the silica xerogel from corn husk and commercial silica xerogel are shown in **Figure 3**. The crystal structure of the as-synthesized xerogel is an amorphous phase as indicated by the shape of a hump in the diffraction pattern at 2θ (theta) of 17–28°.

Breakthrough Analysis

The effect of flow rate on the breakthrough curves of CV and MB is shown in **Figure 4**(**a**) and (**b**). Adsorption was carried out with a flow rate variation of 17, 26, and 29 mL/min, a bed height of 1 cm, and an adsorbate concentration of 10 mg/L. In both CV and MB adsorption, early breakthrough and saturation were obtained at higher flow rates, resulting in a steeper curve than at a slower influent flow rate. As can be seen in **Table 1**, when the flow rate increases, the mass transfer rate increases, promoting higher adsorption capacity (Sen et al., 2002). However, the contact time between adsorbent and adsorbate is getting shorter at higher flow rates, resulting in lower % removal.

The effect of bed height on the breakthrough curve is shown in **Figure 5**(**a**) and (**b**) for CV and MB, respectively. Adsorption was carried out with a bed height of 1 cm, 3 cm, and 5 cm with a flow rate of 17 mL/min and an adsorbate concentration of 10 mg/L. In CV and MB adsorption, the breakthrough curve for bed heights is 1 cm is steeper than those of 3 and 5 cm. A shorter bed means a shorter mass transfer zone is developed in the column, so the saturation time (t_s) will be reached more quickly. The widening of the

breakthrough curve at 5 cm is suspected to be caused by near-wall channeling and higher pressure drop (Tobis & Vortmeyer, 1991). As shown in Table 1, the adsorption capacity also increases at higher bed heights due to more available surface area to promote a higher rate of diffusion and mass transfer. On the other hand, the increase of the bed height can result in higher pressure drops which may lead to uneven flow distribution, therefore reducing mass transfer and dye removal efficiency.

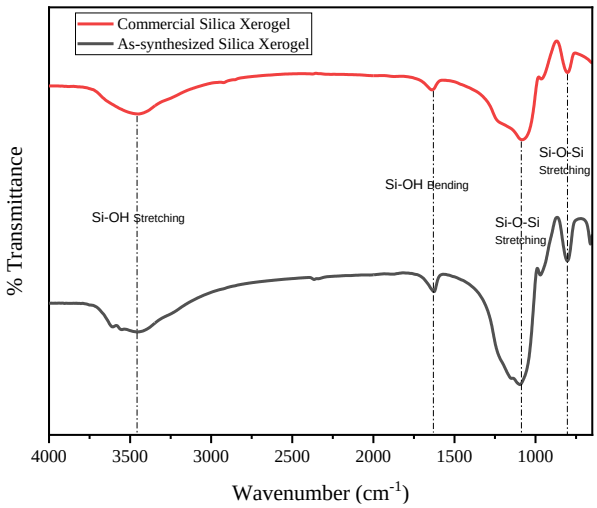

Figure 2. FTIR spectra comparison.

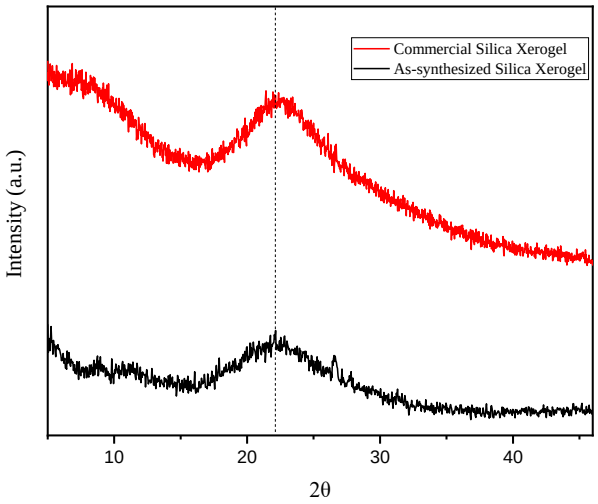

Figure 3. XRD pattern comparison.

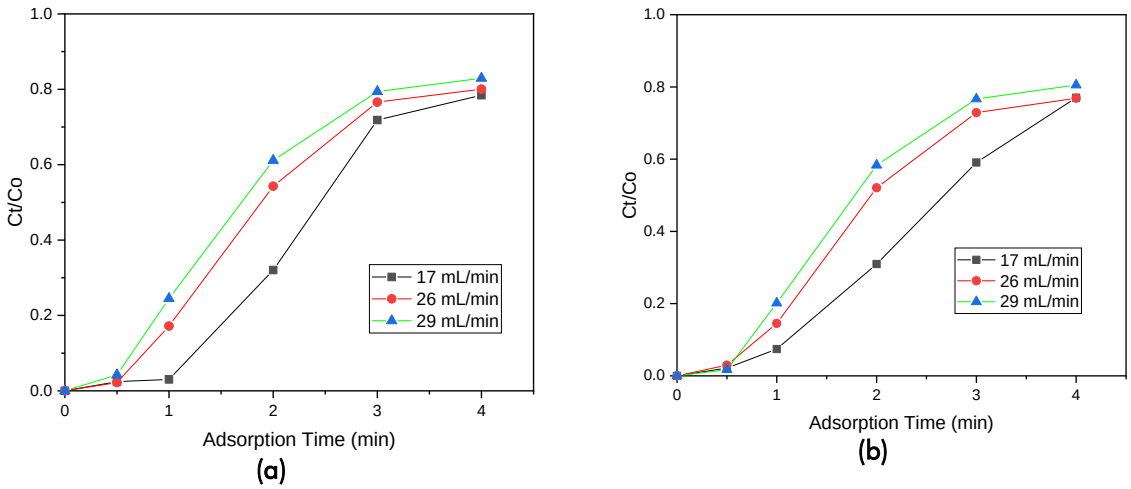

Figure 4. The breakthrough curve for the adsorption of **(a)** crystal violet (CV) and **(b)** methylene blue (MB) on silica xerogel at different flow rates.

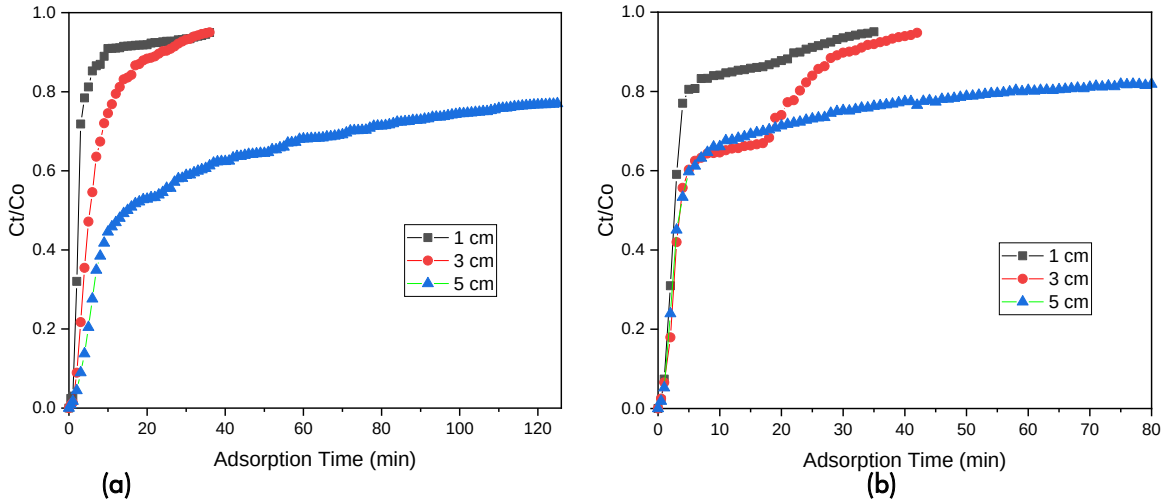

Figure 5. The breakthrough curve for the adsorption of **(a)** crystal violet (CV) and **(b)** methylene blue (MB) on silica xerogel at different bed heights.

Table 1 Adsorption column parameters

Bed Height (cm)	Flow rate (mL/min)	Crystal Violet				Methylene Blue				Pressure Drop (Pa)
		q_{total} (mg)	m_{total} (mg)	%removal	q_e (mg/g)	q_{total} (mg)	m_{total} (mg)	%removal	q_e (mg/g)	
1	17	0.318	0.624	51.005	1.048	0.405	0.611	66.204	1.332	694.557
1	26	0.343	0.714	47.991	1.128	0.518	0.925	56.056	1.707	1082.56
1	29	0.343	0.793	43.244	1.129	0.529	0.848	62.449	1.743	1215.02

Flow rate (mL/min)	Bed Height (cm)	Crystal Violet				Methylene Blue				Pressure Drop (Pa)
		q_{total} (mg)	m_{total} (mg)	%removal	q_e (mg/g)	q_{total} (mg)	m_{total} (mg)	%removal	q_e(mg/g)	
17	1	0.318	0.624	51.005	1.048	0.405	0.611	66.204	1.332	694.557
17	3	0.954	1.707	55.883	1.047	1.361	3.242	41.997	1.494	2083.67
17	5	6.859	18.868	36.352	4.573	2.035	6.021	33.802	1.357	3472.79

Thomas Model Analysis

The fitting of CV and MB adsorption data on silica xerogel from corn husk against linearized Thomas/BA model are displayed in **Figure 6** and **7**. The model parameters, maximum adsorption capacity (q_0), and rate constant (k_{TH}) are summarized in **Table 2**. In general, both CV and MB adsorption data at different flow rates are found to be in a close relationship with the Thomas/BA model as indicated by their R^2 values. With the increase of flow rates, k_{Th} values tend to increase for both CV and MB. The adsorption capacity (q_0) initially increases with flow rate, however after 29 mL/min the value tends to stagnate, which indicates that all adsorbent sites are already occupied (Garg, 2004). The same can be observed in MB; although the adsorption capacity of the column is still rising at 29 mL/min, mass transfer is slowing down.

On the other hand, CV and MB adsorption data show looser correlations with the Thomas/BA model at higher bed heights. Thomas/BA model will fit well at isobaric or at least low-pressure drop column conditions. However, as we can see in **Table 1**, pressure drop increased significantly at higher bed heights.

The maximum adsorption capacities (q_0 and q_e) for CV are higher than MB. The values are 3.400 mg/g (Thomas/BA) and 4.573 mg/g (experimental) for CV compared to 1.977 mg/g (Thomas/BA) and 1.743 mg/g (experimental) for MB. CV and MB are both cationic dyes, which means that they contain positively charged groups. These positive charges enable them to interact with the negatively charged siloxane group in silica xerogel. CV tends to have a higher positive charge compared to MB due to the variations in the substituent groups attached to the central aromatic ring system. CV often contains two or more positively charged quaternary ammonium groups, compared to MB, which usually has only one such group. This difference may cause stronger electrostatic interaction between silica xerogel and CV, therefore resulting in higher adsorption capacity.

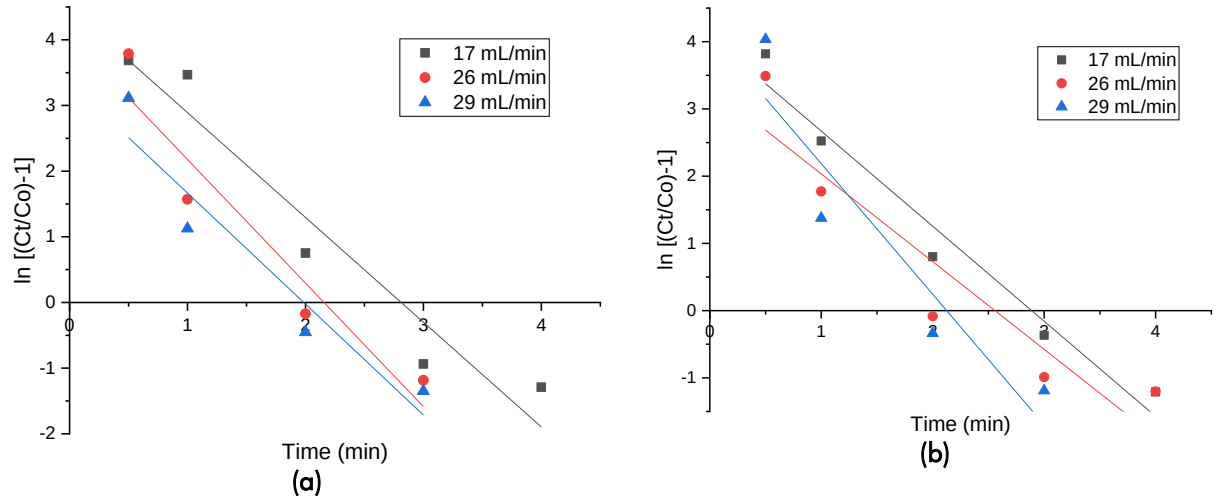

FIGURE 6. Linearized Thomas/BA model for **(a)** crystal violet (CV) and **(b)** methylene blue (MB) at different flow rates.

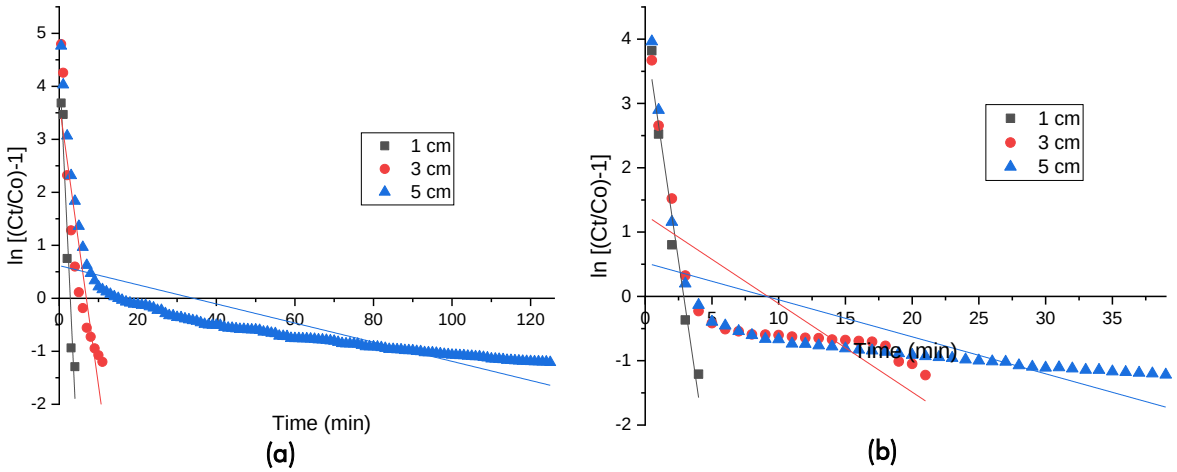

FIGURE 7. Linearized Thomas/BA model for **(a)** crystal violet (CV) and **(b)** methylene blue (MB) at different bed heights.

Table 2 Thomas/BA model parameters.

Thomas Parameter	Flow Rate (mL/min)						Bed Height (cm)					
	Crystal Violet			Methylene Blue			Crystal Violet			Methylene Blue		
	17	26	29	17	26	29	1	3	5	1	3	5
k_{TH} (l/min.mg)	0.174	0.206	0.185	0.157	0.147	0.199	0.174	0.058	0.002	0.157	0.015	0.006
q_0 (mg/g)	1.445	1.691	1.729	1.452	1.947	1.977	1.445	1.176	3.400	1.452	1.557	1.541
q_e(mg/g)	1.048	1.128	1.129	1.332	1.707	1.743	1.048	1.047	4.573	1.332	1.494	1.357
R^2	0.937	0.916	0.916	0.965	0.874	0.873	0.937	0.836	0.519	0.965	0.528	0.417

Yoon-Nelson Model Analysis

The linear experimental data fittings to the Yoon-Nelson model are shown in **Figure 8** and **Figure 9**. These results show a similar tendency to those of Thomas/BA. As summarized in **Table 3**, τ which represents a 50% breakthrough, decreases at a higher flow rate and increases with higher bed height. In a fixed-bed column, a high τ is more desirable because it indicates that more adsorbate can be bound by a particular adsorbent before breakthrough (Solgi et al., 2020).

On the other hand, the Yoon-Nelson rate constant (k_{YN}) varies along the flow rate and decreases with increasing bed height. As was pointed out by Myers et. al. (Myers et al., 2023), the dependency of adsorption uptake coefficients or rate constants value on column parameters could mean that the model does not work under all conditions. The inconsistency of the "adsorption constant" could lead to problems during scale-up. Therefore in the future, a new mathematical model that can describe adsorption data more consistently should be used for evaluation.

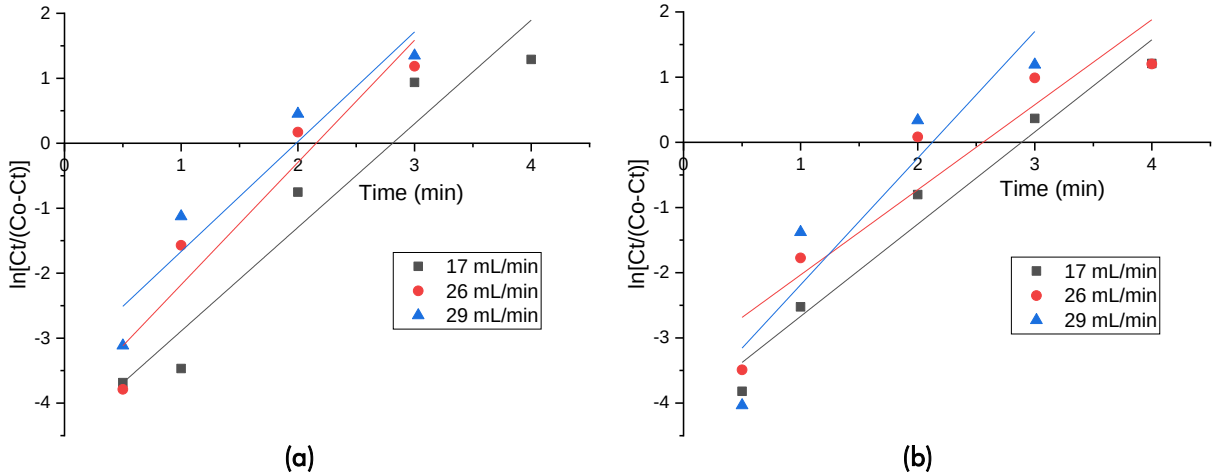

FIGURE 8. Linearized Yoon-Nelson model for **(a)** crystal violet (CV) and **(b)** methylene blue (MB) at different flow rates.

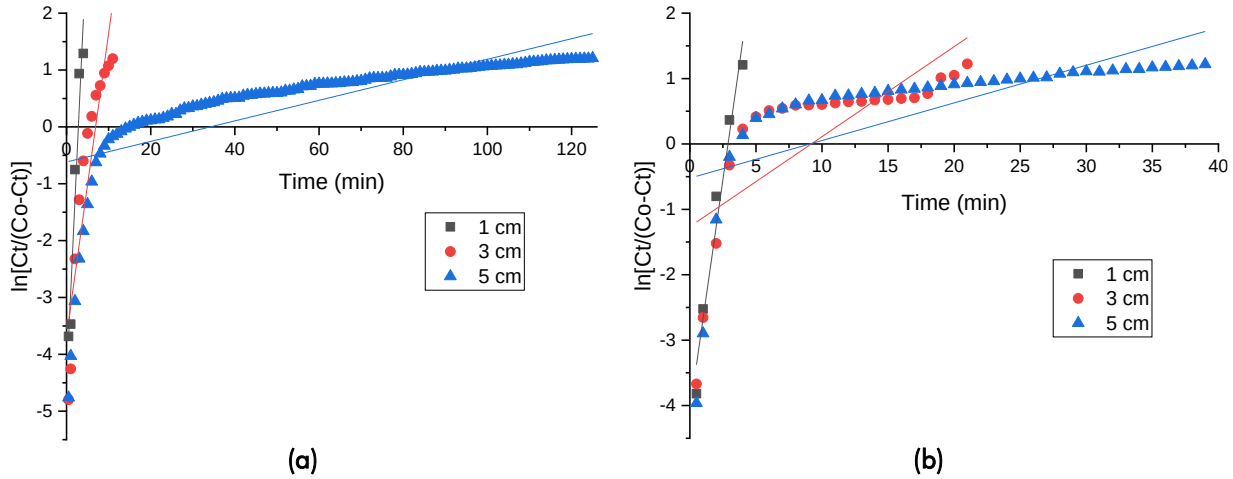

FIGURE 9. Linearized Yoon-Nelson model for **(a)** crystal violet (CV) and **(b)** methylene blue (MB) at different bed heights.

Table 3 Yoon-Nelson model parameters.

Thomas Parameter	Flow Rate (mL/min)						Bed Height (cm)					
	Crystal Violet			Methylene Blue			Crystal Violet			Methylene Blue		
	17	26	29	17	26	29	1	3	5	1	3	5
k_{YN} (min^{-1})	1.595	1.882	1.690	1.414	1.305	1.943	1.595	0.532	0.018	1.414	0.138	0.056
τ (min)	2.812	2.157	1.986	2.888	2.558	2.125	2.812	6.902	34.061	2.888	9.189	9.094
R^2	0.937	0.916	0.916	0.965	0.874	0.873	0.937	0.836	0.5187	0.965	0.528	0.417

CONCLUSIONS

The adsorption capabilities of as-prepared silica xerogel from corn husk in crystal violet and methylene blue in a continuous, fixed-bed column have been investigated. The adsorption capacities of silica xerogel for CV are generally higher than MB at similar conditions. With the increase in flow rate, the mass transfer rate also increases, promoting higher adsorption capacity. However, this caused a shorter contact time between adsorbent and adsorbate, which lowered the % removal. Adsorption capacity also increases at higher bed heights due to more surface area to conduct mass transfer. The results show that CV and MB adsorption in this setup follow Thomas/BA and Yoon-Nelson models at various flow rates, but not so much for bed height variations. The adsorption capacities are still too low compared to similar adsorbent-adsorbate pairs in a batch mode. To reach its full potential in full-scale dye removal from wastewater application, the specification of adsorbent such as shape uniformity and surface area, as well as the fixed-bed column setup, need to be optimized in

the next step of research. The use of alternative mathematical models in experimental data fitting should also be considered to illustrate the column behavior better under various conditions.

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