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Optimizing the two-stage adsorber of NaOH-activated coconut shell carbon for methylene blue removal

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Abstract: This work was aimed at optimizing the adsorbent mass and contact time and evaluating the performance of two-stage batch adsorber of NaOH-activated coconut shell carbon for methylene blue removal. To decrease the dye concentration from 1000 to 89.4 mg/L at any effluent volumes, the two-stage adsorber displays a small mass saving of 0.33% because of the high adsorbent affinity towards methylene blue at 1.80 L/mg. Meanwhile, the contact time can be minimized by 97.6% as opposed to that in one-stage adsorber. The sensitivity analysis of affinity on mass minimization shows a significant saving of 28.5% when the affinity is reduced to 0.01 L/mg. The response surface methodology was used to optimize the two-stage absorber for methylene blue removal, wherein the most significant parameter is the contact time.

Keywords: activated carbon; adsorption; methylene blue; performance evaluation; two-stage adsorber.

1 Introduction

There has been a burgeoning concern over the presence of dyes in water streams. Several techniques for water treatment, which include chemical oxidation, foam flotation, ozonation, biological, photocatalytic, membrane filtration, Fenton and photo-Fenton processes are available for wastewater treatment (Ratan, Kaur, and Adiraju 2018; Yagub et al. 2014). However, they often suffer from high capital and maintenance costs. Among others, activated carbon adsorption has been recognized as effective and cost-competitive treatment for water and air pollution control. Activated carbon has been widely used as adsorbent owing to its highly porous nature that consists of high specific surface and rich functionalities for adsorption of color, odor and contaminants from water (Zubir and Zaini 2020).

The production of activated carbon can be divided into physical and chemical activation. Physical activation involves carbonization of carbonaceous precursor at 400–850 °C in an inert atmosphere, followed by activation of the resulting char at 600–900 °C in the presence of carbon dioxide and/or steam atmosphere. For chemical activation, the feedstock is impregnated with dehydrating agent, followed by activation under anoxic environment (Ming-Twang et al. 2015). Activators such as phosphoric acid, zinc chloride, potassium carbonate and sodium hydroxide are commonly applied in chemical activation to encourage pyrolytic decomposition and inhibit the formation of tar, thus enhancing the yield of activated carbon (Amran and Zaini 2020). To produce low-cost activated carbon, agricultural residues like banana peel, orange peel, peanut shell and coconut shell could be considered as sustainable feedstock. They are abundantly available with no added-value and are often discarded or left to decay with time. These are carbonaceous materials which can be the promising alternative for conventional activated carbon. In addition, the use of eco-friendly materials will aid in managing the solid waste pollution and cutting the production cost of activated carbon.

A single-stage adsorber is often utilized to treat dye-containing wastewater, and it has been accepted as standard protocol in adsorption studies (Zubir and Zaini 2020). However, the setting is incapable to predict the optimum mass and contact time, and also the removal performance at different volumes and concentrations to satisfy the large-scale operation. Oladipo and Ifebajo (2018) reported an

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improvement of tetracycline removal by magnetic chicken bone biochar from 93% in single-stage adsorber to 96% in two-stage adsorber. In a related work, the equilibrium time for acid red 25 decreased from 895 min in single-stage adsorber to 401 min in two-stage adsorber (Oladipo and Gazi 2015). Similar findings were recently reported in literature (Bamatraf and Zaini 2021; Hijab et al. 2020; Palanisami et al. 2021). Nonetheless, the adsorptive properties of these adsorbents are limited only to certain pollutants of interest. To widen the research horizon, the present work was aimed at designing a two-stage adsorber of NaOH-activated coconut shell carbon that exhibits the outstanding performance and affinity for methylene blue removal in one-stage adsorber (Cazetta et al. 2011). The data on two-stage adsorber design for this adsorbent are still unavailable in literature, thus worth to be exploited for the wastewater treatment application. The optimum adsorbent dosage and contact time, and the most significant parameter of two-stage adsorber were reported. The performance evaluation was discussed to shed better understanding on the advantageous of two-stage adsorber of NaOH-activated coconut shell carbon for industrial dye-bearing wastewater treatment.

2 Methods

Isotherm and kinetic constants of one-stage adsorber were taken from Cazetta et al. (2011). The optimization of two-stage adsorber design using Langmuir isotherm and pseudo-second-order kinetic models was performed using Microsoft Excel (Hijab et al. 2020; Mohammed et al. 2012). Table 1 summarizes the isotherm and kinetic constants.

Table 1: Langmuir and pseudo-second-order constants (Cazetta et al. 2011).

Langmuir model		Pseudo-second-order model	
q_m (mg/g)	b (L/mg)	q_e (mg/g)	K_2 (g/mg min)
916	1.8	911	0.00092

The schematic diagram of a two-stage adsorber is shown in Figure 1.

Methylene blue solution at initial concentration C_o (mg/L) and volume L_s (dm^3) enters the stage 1, wherein S_{s1} (g) coconut shell activated carbon is added to reduce the concentration to C_1 (mg/L). In stage 2, the effluent is further treated with S_{S2} (g) of activated carbon to meet the final equilibrium concentration of C_2 (mg/L). The mass balance relationship in each stage can be generally presented as,

$$q_n = \frac{L_s}{S_{sn}}(C_{n-1} - C_n) \tag{1}$$

where q_n (mg/g) is the amount of dye adsorbed at stage n.

The equilibrium and kinetics of methylene blue adsorption onto NaOH-coconut shell carbon obeyed Langmuir and pseudo-second-order models. Hence, these equations were employed in the optimization of mass and contact time in two-stage adsorber design. The Langmuir isotherm is given as,

$$q_n = \frac{q_m b C_n}{1 + bC_n} \tag{2}$$

where, q_m (mg/g) is the methylene blue capacity at monolayer saturation and b (L/mg) is the adsorption affinity. Substituting Eq. (2) into Eq. (1) and rearrange, allows the determination of adsorbent mass in each stage,

$$S_{sn} = \frac{L(C_{n-1} - C_n)}{bq_m C_n / 1 + bC_n} \tag{3}$$

The pseudo-second-order model is given as,

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \tag{4}$$

where q_t (mg/g) is the adsorbent capacity at time t (min) and K_2 (g/mg min) is the rate constant. Substituting Eq. (4) into Eq. (1) and rearrange, allows the determination of contact time in each stage,

$$t_n = \frac{\left(1/q_e K_2\right) L_s (C_o - C_e)}{S_{sn} q_e + L_s (C_o - C_e)} \tag{5}$$

In the experimental work, one-stage adsorber was performed using 25 mL of methylene blue solution at varying concentrations and 25 mg of activated carbon. In the simulation of two-stage adsorber, the highest C_o is 1000 mg/L and different volumes of 25–1000 mL were introduced to mimic the upscaling of two-stage adsorption system. In stage 1 of the two-stage adsorber, a series of step-size decrement in dye

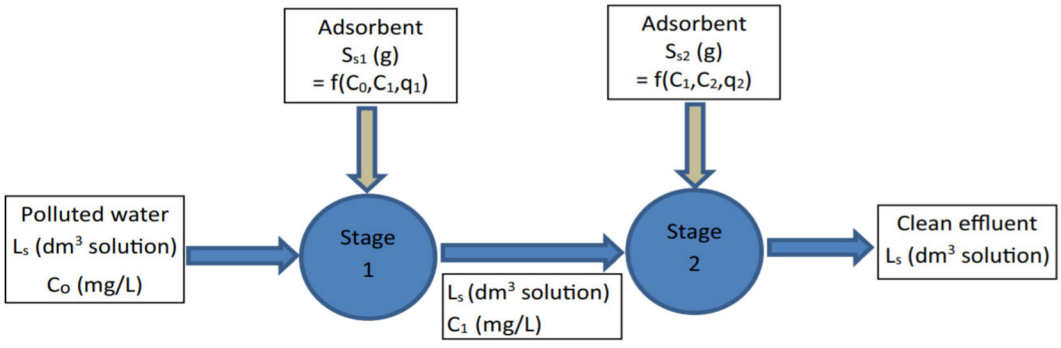

Figure 1: Schematic diagram of two-stage adsorber (Hijab et al. 2020).

concentration from 1000 mg/L to C_e = 89.4 mg/L was structured for each consecutive sorption system. The mass of activated carbon was calculated for each decrement. For example, in sorption system number 1, the design objective is to reduce the initial dye concentration from 1000 to 950 mg/L. Similarly in sorption system numbers 2, 3, and so on, the design objectives are to reduce the initial dye concentration from 950 to 900 mg/L, 900 to 850 mg/L, and lastly down to 89.4 mg/L. While, in stage 2, the design objective for sorption system number 1 is to reduce the concentration from 950 to 89.4 mg/L. The same approach applies for determination of minimum contact time for two-stage adsorber.

Total mass of adsorbent to complete the removal in two-stage adsorber is expressed as,

$$\frac{S_1 + S_2}{L} = \frac{C_O + bC_OC_1 - C_1 - bC_1^2}{q_m bC_1} + \frac{C_1 + bC_1C_2 - C_2 - bC_2^2}{q_m bC_2} \tag{6}$$

and setting,

$$\frac{d\,(S_1 + S_2)/L}{dC_1} = 0 \tag{7}$$

to yield,

$$0 = \frac{-q_m b^2 C_1^2 - q_m bC_O}{(q_m bC_1)^2} + \frac{1 + bC_2}{q_m bC_2} \tag{8}$$

rearranging and solving,

$$\frac{C_o}{C_1^2} = \frac{1}{C_2} \tag{9}$$

The removal percentage, R was calculated by the following equation.

$$R = 100\left(\frac{C_o - C_2}{C_o}\right) \tag{10}$$

Different removal rates and final concentrations in the effluent were set to allow the performance evaluation of two-stage adsorber at optimal mass using Eqs. (6), (9) and (10). The most significant parameter and confidence level were analyzed by response surface methodology (RSM) of Minitab 17 Statistical software. A 2-level factorial experimental design of RSM was employed to optimize the two-stage adsorber in achieving a cost-competitive methylene blue removal.

3 Results and discussion

3.1 Optimum mass and contact time

Figure 2 displays the minimum mass required to achieve the capacity of 916 mg/g in two-stage adsorber for effluent volume of 25 mL and methylene blue concentration of 1000 mg/L. The minimum mass was recorded at sorption system 15 as 24.92 mg, which renders a saving of 0.33%. To treat a 25 mL effluent, the stage 1 needs 19.1 mg of

Table 2: Minimum adsorbent required for one-stage and two-stage adsorbers.

Volume of methylene blue (mL)	25	100	500	1000
Minimum mass in two-stage (mg)	24.9	99.7	498	997
Actual mass in one-stage (mg)	25	100	500	1000
Saving in mass (mg)	0.08	0.33	1.67	3.33
Percentage saving (%)	0.33	0.33	0.33	0.33

Table 3: Effect of adsorption affinity on percentage saving of adsorbent mass in two-stage adsorber (V = 1000 mL).

Adsorption affinity, b (L/mg)	0.01	0.05	0.1	1.8
Minimum mass in two-stage (mg)	1506	1096	1045	997
Actual mass in one-stage (mg)	2105	1216	1105	1000
Mass saving (mg)	600	120	60	3.33
Percentage saving (%)	28.5	9.87	5.43	0.33

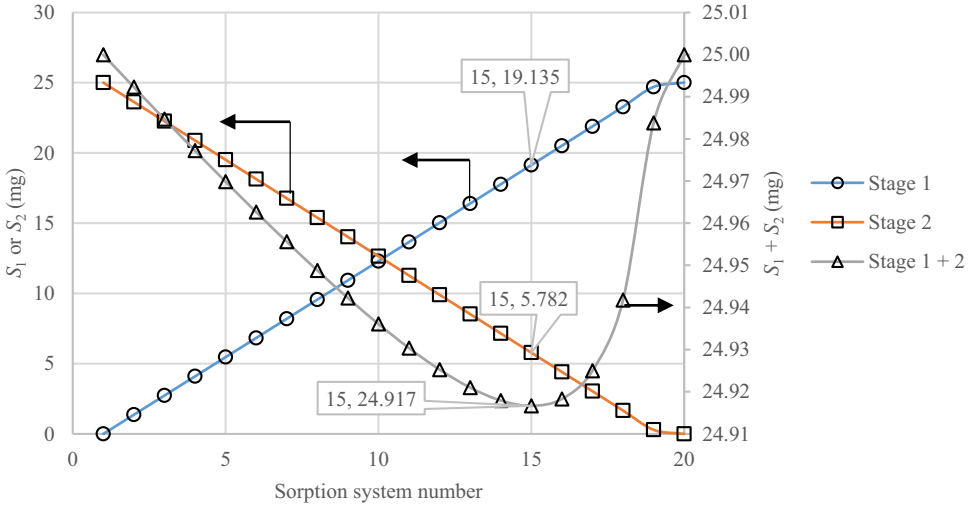

Figure 2: Mass optimization in two-stage adsorber of coconut shell activated carbon for the treatment of 1000 mg/L methylene blue dye in 25 mL solution.

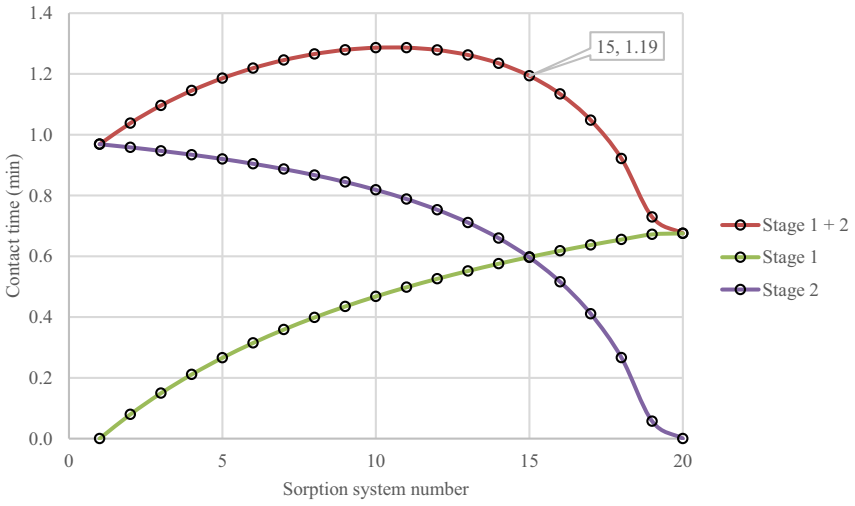

Figure 3: Time taken to treat 1000 mg/L methylene blue dye in 25 mL solution using two-stage adsorber of coconut shell activated carbon.

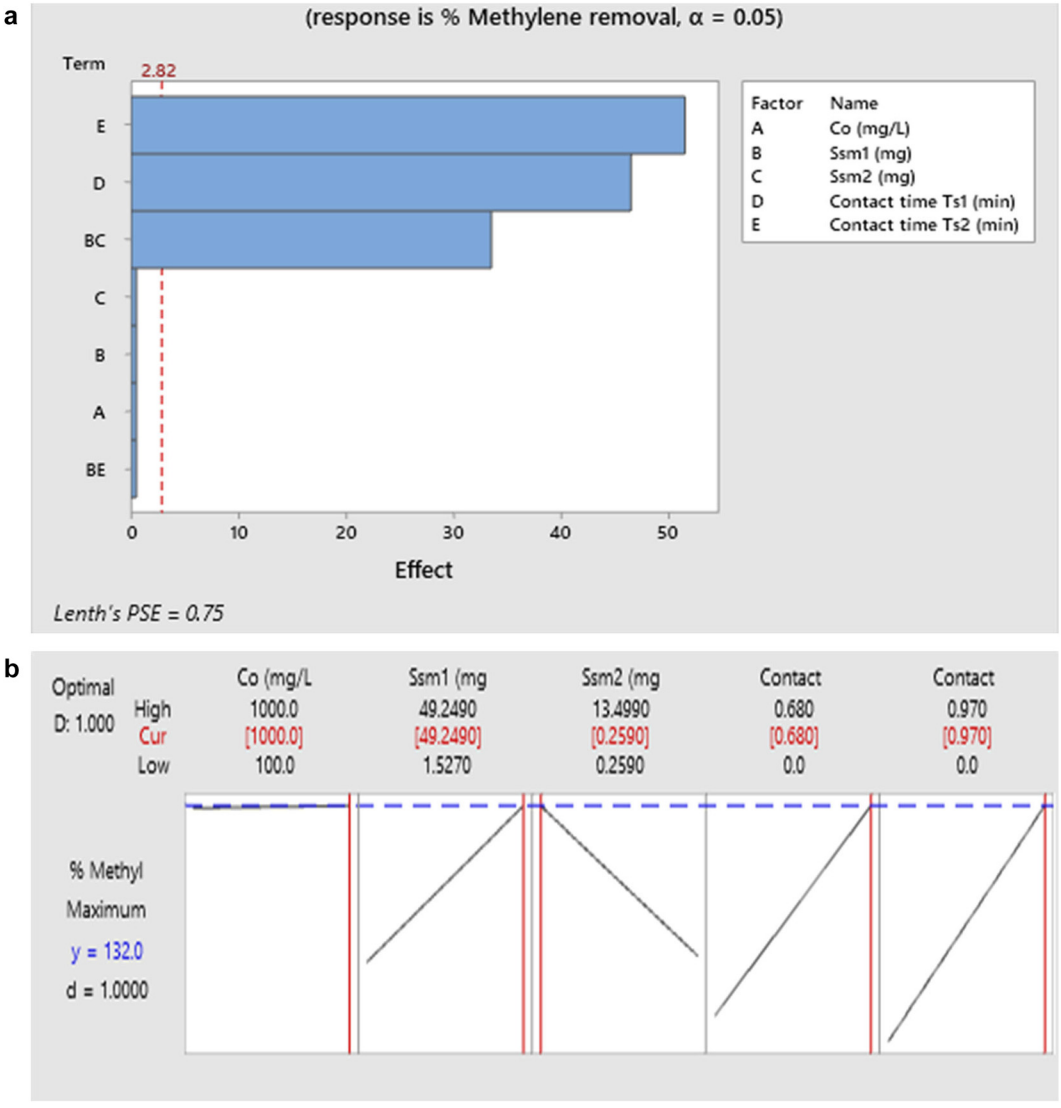

Figure 4: (a) Pareto chart and (b) optimization plot of the effect in two-stage adsorber of coconut shell activated carbon for the treatment of 1000 mg/L methylene blue dye in 25 mL solution.

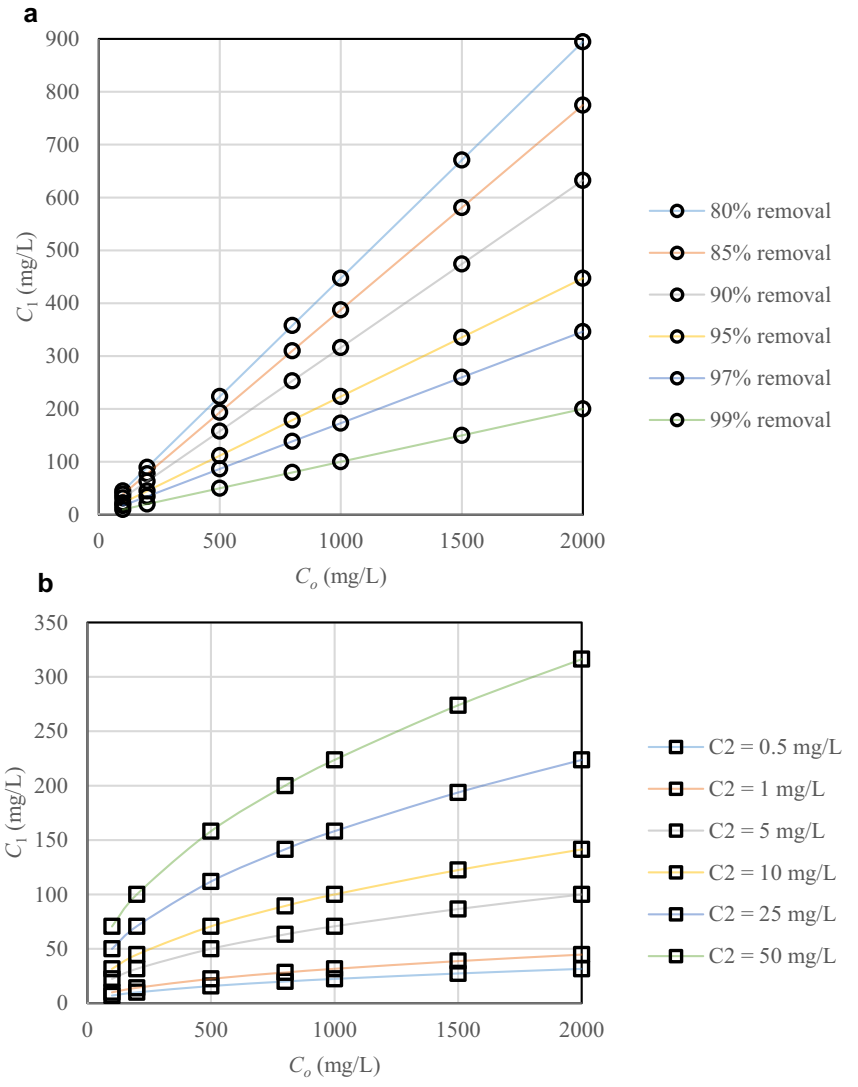

Figure 5: Effects of initial concentration, C_o on intermediate concentration, C_1 at various (a) removal percentages and (b) equilibrium concentrations, C_2.

activated carbon, at which the concentration subsides from 1000 to 300 mg/L, while the stage 2 consumes only 5.78 mg to complete the adsorption at equilibrium concentration of 89.4 mg/L. The amount of adsorbent is always higher at stage 1 because of the high concentration gradient requirement for decreasing the load in stage 2 to reach equilibrium. This holds for any effluent volumes. Table 3 summarizes the saving in activated carbon mass at different effluent volumes. Clearly, the deviation in mass widens as the effluent volume increases. This highlights the advantageous of two-stage adsorber to meet the same performance at large-scale treatment of dye-containing effluent (see Table 2).

The percentage saving is small because of the high adsorption affinity, b of NaOH-coconut shell carbon towards methylene blue. Affinity can be defined as to the equilibrium ratio of the solid phase solute concentration (mol/mg) to the liquid phase solute concentration (mol/L). The higher the affinity, the greater the solid phase concentration as comparison to that in the bulk solution, which reflects the effectiveness of adsorbent to remove dye from water. A sensitivity analysis was performed to visualize the effect of affinity on adsorbent mass to treat 1000 mL dye effluent in a two-stage adsorber. The affinity values were arbitrarily decreased, and the pattern is summarized in Table 3. Noticeably, the decrease in affinity increases the gap between the mass required in one-stage adsorber and that in two-stage adsorber. For adsorbent with low affinity, more sites are needed to improve the interaction probabilities between methylene blue molecules and adsorbent surface, which can only be realized by adding the mass. Conversely, the difference is small for a high affinity adsorbent as demonstrated in this work. Nonetheless, the amount of adsorbent can be significantly minimized by means of two-stage adsorber design for a cost-competitive process from an economic perspective.

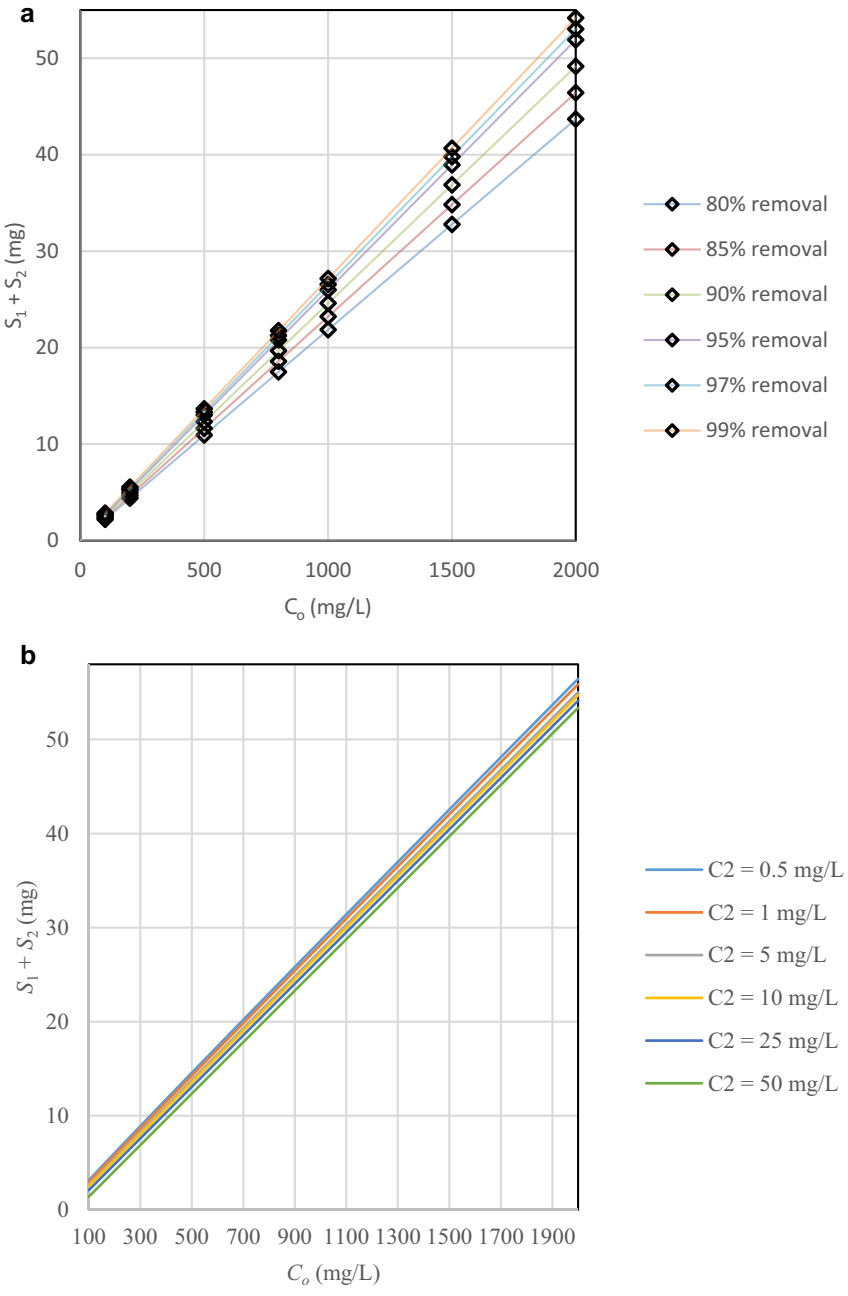

Figure 6: Effects of initial concentration, C_o on optimum mass, $S_1 + S_2$ at various (a) removal percentages and (b) equilibrium concentrations, C_2.

The respective dosages at stage 1 and stage 2 at optimum mass of coconut shell activated carbon were used to simulate the time taken to meet the removal of 916 mg/g methylene blue in 25 mL effluent bearing the concentration of 1000 mg/L. The total contact time at every sorption system number in the two-stage adsorber is shown in Figure 3. The optimum contact time was recorded at sorption system 15 as 1.2 min. The decrease in concentration, C_o from 1000 to 300 mg/L in stage 1 of two-stage adsorber with 19.1 mg adsorbent requires 0.6 min as opposed to 4 min in one-stage adsorber with 25 mg adsorbent (Cazetta et al. 2011). To accomplish the treatment to C_e = 89.4 mg/L, the equilibrium time in two-stage adsorber is 1.2 min, as compared to 50 min in one-stage adsorber, which brings a 97.6% cut in adsorption time. The contact time is longer in one-stage adsorber because the adsorption rate subsides as the concentration gradient diminishes with time, thus slowing down the dye removal. Meanwhile, the split of dosages in the two-stage adsorber is able to sustain the high concentration gradient, thus increasing the rate and reducing the adsorption time.

Figure 4 displays the effect of parameters by RSM. In Pareto chart (Figure 4(a)), any effects that extend beyond the reference line are significant (Lamido, Alhassan, and

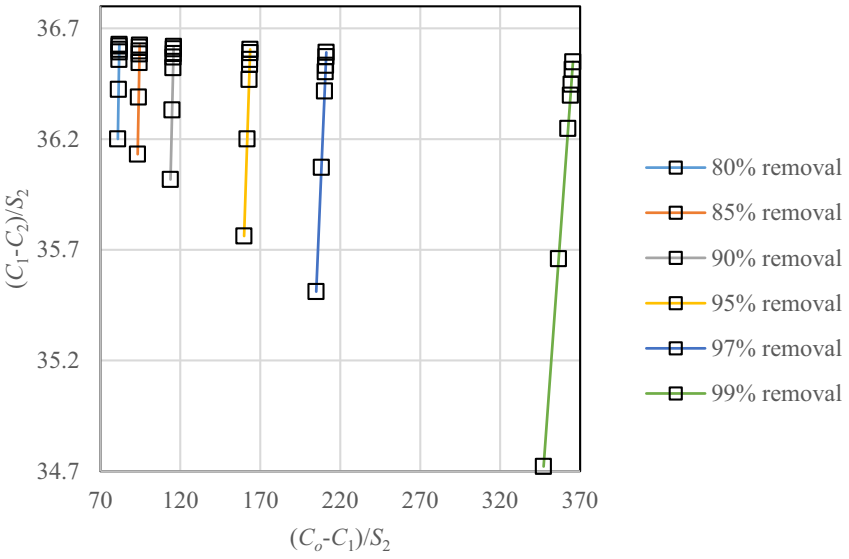

Figure 7: Relationship between concentration gradient in stage 2 against that in stage 1 at targeted removal percentages.

Lawal 2021). Therefore, the most significant parameter in each stage of adsorber is the contact time. This is in line with the analysis of variance (ANOVA table is not shown), where the contact time shows a p-value <0.05. From the optimization plot (Figure 4(b)), a 100% removal of methylene blue at C_o = 1000 mg/L in 25 mL solution can be achieved at the optimum contact times of 0.68 and 0.97 min in stages 1 and 2 are, respectively, with the optimum adsorbent dosages of 49.3 and 13.5 mg, respectively. When d value is equal to 1, it statistically indicates a 100% removal efficiency. Thus, a 99% methylene blue removal was attained using the two-stage adsorber based on a 95% confidence level.

3.2 Performance evaluation

Figure 5 exhibits the effects of initial concentration, C_o on intermediate concentration leaving stage 1, C_1 at different removal percentages and equilibrium concentrations, C_2. The linear lines display a decrease in gradient as the removal percentage increases to 99%. Also, the magnitude of C_1 decreases as the removal percentage increases. Similarly, C_1 increases as the target equilibrium concentration increases. A small C_1 signifies a larger load of activated carbon used in stage 1 to allow the adsorption of remaining effluent in stage 2 at low equilibrium. The profiles provide useful insight into the effectiveness of a two-stage adsorber to be employed at industrial scale to accomplish a bigger removal percentage of concentrated dye effluent.

Figure 6 depicts the effects of initial concentration on total mass for different removal percentages and equilibrium concentrations in two-stage adsorber. The simulation was executed at effluent volume of 25 mL. The same patterns could also be expected for any effluent volumes. Generally, the higher removal percentage demands for more quantity of activated carbon to attain the desired separation. The variation in dosage to meet the target removal percentage is not significant at low initial concentrations between 20 and 200 mg/L.

The changes in mass requirement can be seen for different removal percentages as the concentration rises to 2000 mg/L. However, the gap in optimum dosage is still narrowed for 95–99% removal, implying the effectiveness of adsorbent to overcome the mass transfer resistance in liquid phase at high concentration gradient. A rising trend is also depicted in Figure 5(b), unlocking the parallel trend of optimum mass in two-stage adsorber, which increases with initial concentration.

Figure 7 illustrates the relative removal at stage 2 against that at stage 1. Obviously, stage 1 exhibits a greater efficiency for dye removal than stage 2 because the former endows a higher concentration gradient to boost the separation. Often, stage 2 is operating at low equilibrium to reach the final concentration. The efficiency at stage 2 increases with equilibrium concentration for any removal rates. It suggests that the overall efficiency of a two-stage adsorber is significant in stage 2 at low removal percentage.

4 Conclusions

Two-stage adsorption system was designed to optimize adsorbent mass and contact time for methylene blue removal by NaOH-activated coconut shell carbon. The

decrease in mass is only 0.33% because of the excellent affinity of activated carbon towards methylene blue. The sensitivity analysis forecasts a 30% decrease in mass if the affinity is 0.01 L/mg. On top of that, the time taken to attain the equilibrium in two-stage adsorber was considerably minimized from 50 min to approximately 1.2 min. The two-stage adsorber capitalizes the use of adsorbent for overall adsorption performance and reduces the costs of operation. The range of optimal conditions by response surface methodology is essential for the flexibility of the adsorption process. The performance evaluation provides better insights into the scaling-up of two-stage adsorber for industrial dye-containing wastewater treatment.

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