INSIGHT INTO THE OPTIMIZATION OF MASS AND CONTACT TIME IN TWO-STAGE ADSORBER DESIGN FOR MALACHITE GREEN REMOVAL BY COCONUT SHELL ACTIVATED CARBON

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ABSTRACT

The present work was aimed at evaluating the traits of a two-stage adsorber in optimizing the mass and contact time to achieve the desired removal performance. Data from literature for malachite green removal by coconut shell activated carbon in one-stage batch adsorber were taken as the basis for the simulation. Results show that the activated carbon mass was reduced by 22.4%, i.e., from 0.1 g to 0.078 g for 100 mL effluent, while the contact time was minimized from 30 min to 1.43 min for the removal of 50 mg/L dye in the two-stage adsorber. In the performance evaluation, the activated carbon mass in stage-1 is higher than that in stage-2 to lessen the load in accomplishing the removal at minimum dosage. The findings suggest that the two-stage adsorber design is economically viable for removing the dye in wastewater treatment.

Keywords: *Coconut shell activated carbon, malachite green, two-stage adsorber, mass optimization, time optimization*

INTRODUCTION

Activated carbon can be produced from carbonaceous materials, such as coconut shell, nutshell, coal, peat, and wood. The primary precursor of activated carbon is any organic material with high carbon content. The preferable alternative is agricultural wastes, as they are abundantly available at no cost. Agricultural residues such as rice husk [1], coconut shell [2], and oil palm ash [3] have been reported as promising feedstock of activated carbon. Coconut is an important agricultural product and is currently ranked fourth in terms of total planting area in Malaysia [4]. Consequently, it offers a sustainable supply of coconut shells to produce activated carbon.

More than 10,000 dyes have been used in textile, paper, rubber, plastics, leather, cosmetic, pharmaceutical, and food industries [5]. Dye-containing effluent often finds its ways to water streams due to inadequate treatment measures and waste management system. The presence of dye in water blocks the transmission of sunlight and inhibits photosynthetic activity, thereby reducing dissolved oxygen for plant growth and respiration [6]. Dyes of complex structure and synthetic origin are purposely designed to withstand the breakdown with time, and exposure to sunlight, water, soap, and oxidizing agents [7],[8]. Consequently, the conventional treatment methods such as flocculation [9], membrane filtration [10],[11], and advanced oxidation [12] are less effective and not practically viable because of the high operating and maintenance costs [13].

Activated carbon adsorption is a preferred dye-bearing wastewater treatment method owing to its high efficiency, low-cost, simple operation, and easy to scale-up [14]. Activated carbon endows a large specific surface to improve interaction probabilities with dye molecules in water, thus enhancing the uptake capacity [15]. However, the price of activated carbon is not cheap. The mass of adsorbent in one-stage batch adsorber is not fully capitalized in achieving the desired removal performance. A two-stage adsorber design is proposed to minimize the adsorbent mass and contact time for the dye adsorption process to be economically sound.

The advantages of two-stage adsorber have been highlighted in some research works. For a 99% removal of 300 mg/L methylene blue by tea leaf, the contact times are 18 min in stage-1 and 10.1 min in stage-2, which brings a total of 28.1 min as opposed to 60 min in one-stage adsorber [16]. Similarly, sawdust demonstrates a 99% removal in 37.54 min (26 min in stage-1 and 11.54 min in stage-2) in two-stage adsorber, as compared to 100 min in one-stage adsorber [17]. The present work is aimed to expand the knowledge boundary to optimize the mass and contact time for malachite green dye removal by coconut shell activated carbon in two-stage adsorber [18]. The performance was discussed to shed light towards sustainable industrial applications.

METHODS

Adsorption data from [18] were used to model two-stage adsorber. Table 1 summarizes the Langmuir and pseudo-second-order constants.

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Table 1 Langmuir and pseudo-second-order constants [18]

Langmuir model				Pseudo-second-order model		
q_m (mg/g)	K_L (L/mg)	R^2		q_e (mg/g)	k_2 (g/mg.min)	R^2
70.8	1.64	0.997		44.5	0.0176	0.864

The simulation was performed using Microsoft Excel. The Langmuir equation is given as [19],

$$q_e = \frac{q_n K_L C_e}{1 + K_L C_e} \tag{1}$$

where, q_e (mg/g) is the capacity at equilibrium, q_m (mg/g) is the maximum capacity at surface saturation, C_e (mg/L) is the equilibrium concentration, and K_L (L/mg) is the sorption affinity. The pseudo-second-order equation is given as [20],

$$q_t = \frac{q_n^2 k_2 t}{1 + q_e k_2 t} \tag{2}$$

where q_t (mg/g) is the capacity at any time, t (min) and k_2 (g/mg.min) are the rate constant.

Figure 1 shows the schematic of the two-stage batch adsorption process.

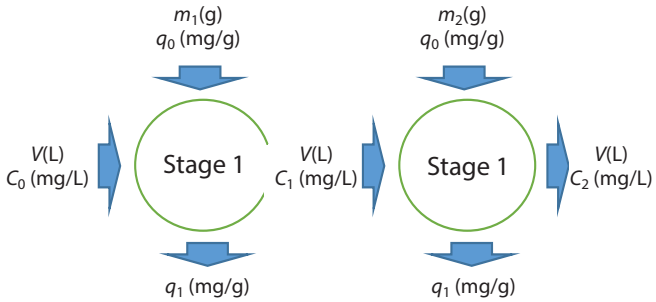

Figure 1 Two-stage adsorber design

From Figure 1, each stage treats the same volume V(L), and different masses of m_1 (g) and m_2 (g) are needed to meet the desired removal capacities (mg/g), q_1, and q_2. The initial adsorption capacity entering each stage, q_o (mg/g) = 0. The concentration of dye in solution decreased initially from C_0 (mg/L) to intermediate concentration C_1(mg/L) in stage-1 and then to C_2 (mg/L) at equilibrium in stage-2. The material balance for each stage can be written as,

$$V(C_0 - C_1) = m_1(q_1 - q_2) \tag{3}$$

$$V(C_1 - C_2) = m_2(q_2 - q_0) \tag{4}$$

The design objective was to treat 100 mL of malachite green solution at initial concentration, C_0 = 50 mg/L. A series of equilibrium concentration, C_1 from 50 mg/L to 1.34 mg/L [18] in a 2.5 mg/L step-size (sorption system number) was considered in stage-1 (sorption system 1, step-size = 0; sorption system 2, step-size = 2.5 mg/L, and so on). The volume, V was varied between 100 mL and 300 mL to observe its effect on optimum adsorbent mass.

By substituting Equation 1 into Equation 3, the material balance as a function of Langmuir constants at each stage can be rewritten as,

$$\frac{m_1}{V} = \frac{(C_0 - C_1)(1 + K_L C_1)}{q_m K_L C_1} \tag{5}$$

$$\frac{m_2}{V} = \frac{(C_1 - C_2)(1 + K_L C_2)}{q_m K_L C_2} \tag{6}$$

$$\frac{m_1 + m_2}{V} = \frac{1}{q_m K_L} = \left(\frac{(C_1 - C_2)(1 + K_L C_2)}{C_1} + \frac{(C_1 - C_2)(1 + K_L C_2)}{C_1} \right) \tag{7}$$

Equation 7 was differentiated against C_1, where $\frac{d(m_1 + m_2)/V}{dC_1}$ to give,

$$C_1 = (C_0 C_2)^{\frac{1}{2}} \tag{8}$$

The optimum mass for each stage can be computed by Equations 7 and 8.. Different removal rates (80% to 99%) and final concentrations (0.5 mg/L to 10 mg/L) in the effluent were set to allow the performance evaluation of the two-stage adsorber.

By substituting Equation 2 into Equation 3, the expression for contact time required to achieve the desired removal by minimum adsorbent mass is,

$$t = \frac{\left(\frac{1}{q_e k_2}\right) V(C_o - C_t)}{m q_e - V(C_o - C_t)} \tag{9}$$

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

$$R = 100\left(\frac{(C_0 - C_2)}{C_0}\right) \tag{10}$$

RESULTS AND DISCUSSION

Figure 2 displays the profiles of adsorbent mass at different effluent volumes in a two-stage adsorber.

Generally, the amount of coconut shell activated carbon increased to satisfy the same removal performance with increasing volume of effluent. For a two-stage adsorber, the minimum adsorbent mass was estimated at sorption system 17. As the solution volume rises from 100 mL to 300 mL, the minimum mass values are 0.078 g, 0.116 g, 0.155 g, 0.194 g, and 0.233 g, respectively. It is noted that the difference between the mass used in one-stage adsorber (sorption system 1) and that of two-stage adsorber (at optimum point,

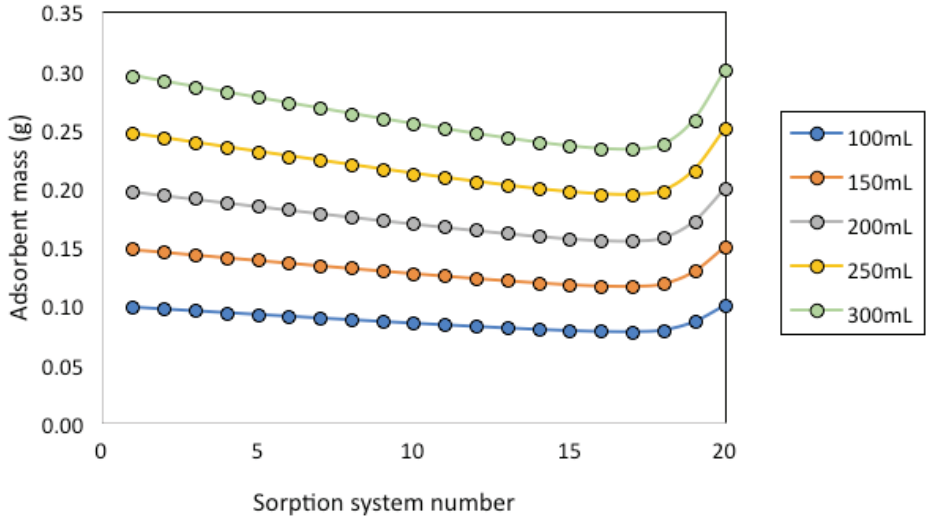

Figure 2 Minimum adsorbent mass required at different volumes of effluent in two-stage adsorber (C_0 = 50 mg/L; C_2 = 1.34 mg/L)

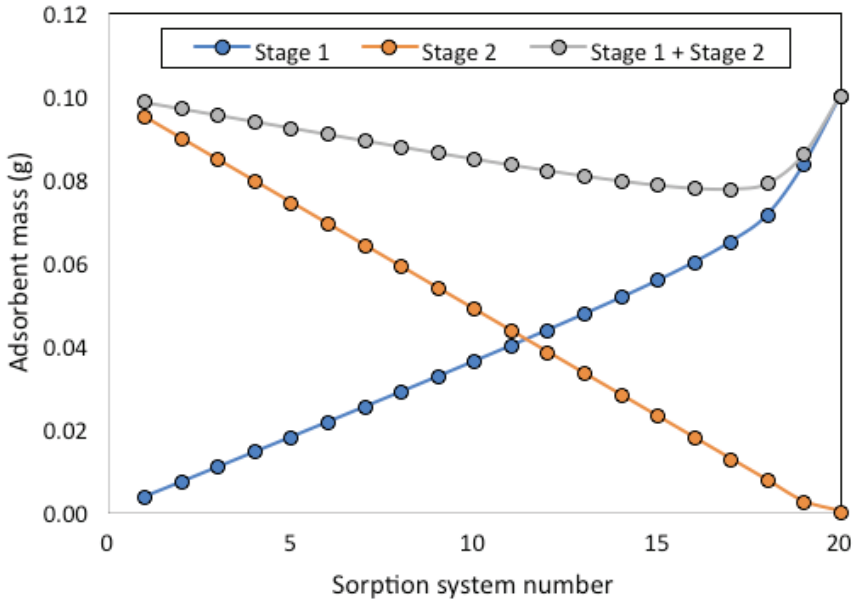

Figure 3 Profiles of adsorbent mass in each stage of a two-stage adsorber (V = 100 mL; C_0 = 50 mg/L; C_2 = 1.34 mg/L)

sorption system 17) is bigger as the volume of effluent increases. Figure 3 shows the mass profiles in each stage of the two-stage batch adsorber to treat 100 mL malachite green effluent. From the combined mass in stage-1 and stage-2, the one-stage batch adsorber (sorption system 1) requires 0.1 g of coconut shell activated carbon, while the mass reduces to 0.078 g in two-stage adsorber (sorption system 17). The saving of adsorbent mass is 22.4%, and this is true for any volumes of effluent to be treated. From Figure 3, at sorption system 17, the mass in stage-1 is 0.065 g, which is greater than that in stage-2 at 0.013 g. It implies that stage-1 is necessary to drive more removal, so less load would be needed to reach equilibrium in stage-2.

Figures 4 and 5 show the relationships between the intermediate concentration, C_1 and the initial concentration, C_0 at different removal percentages and equilibrium concentrations, C_2. From Figure 4, the lines are essentially linear for different percentages of malachite green removal, with the gradient decreases in steepness as the percentage increases from 80% to 99%. Furthermore, C_1 is smaller at 99% removal, and the magnitude increases as the percentage decreases. Similarly, C_1 is low at C_2 = 0.5 mg/L, and the value increases as C_2 increases. A small C_1 is tied up with a larger adsorbent mass used in stage-1 to allow the removal of the remaining dye concentration in stage-2 at low equilibrium. The profiles offer insight into the effectiveness of a two-stage batch adsorber to accomplish a bigger removal percentage for concentrated dye effluent in addition to minimum adsorbent mass.

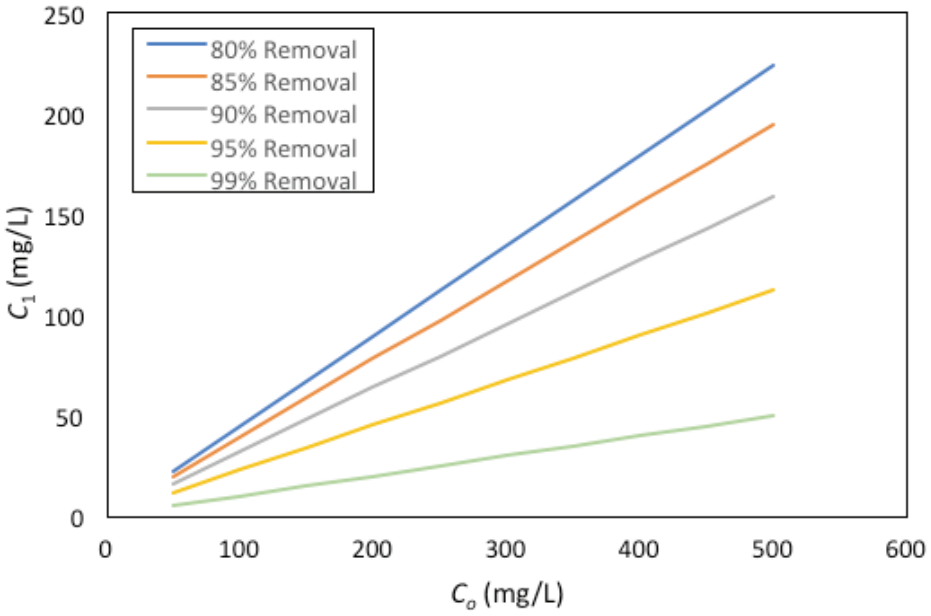

Figure 4 Intermediate concentration, C_1 against initial concentration, C_o at different removal percentages

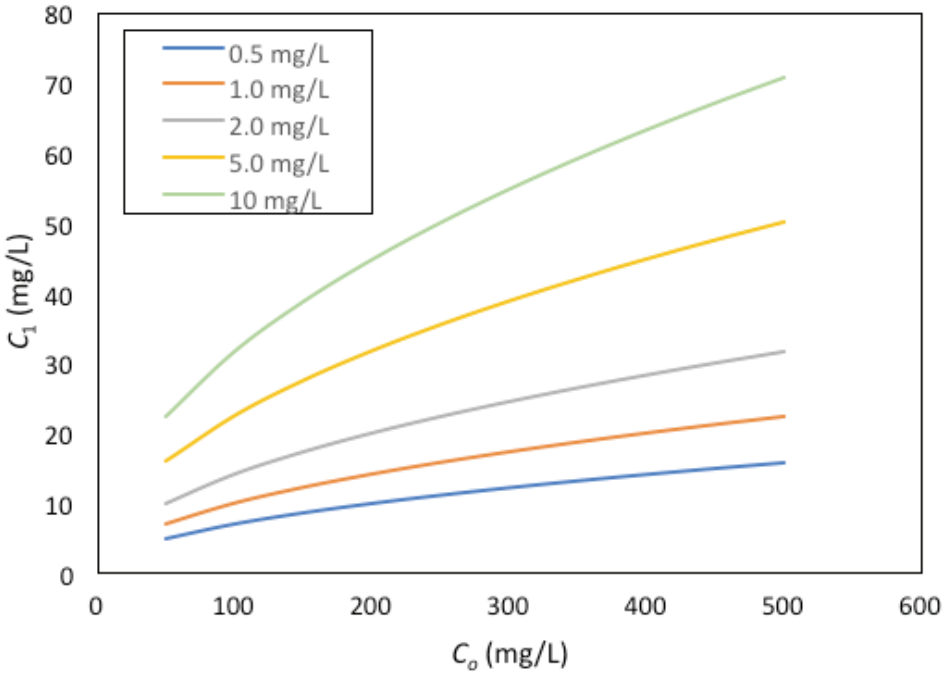

Figure 5 Intermediate concentration, C_1 against initial concentration, C_o at different targeted equilibrium concentration, C_2

Figures 6 and 7 illustrate the effects of C_o on the total adsorbent mass for different removal percentages and equilibrium concentrations in the two-stage adsorber. The relationship is linearly proportional for 80% to 99% removal of malachite green. The higher the removal percentage, the more the minimum mass of activated carbon would be required. Additionally, there is a huge leap in adsorbent mass to meet the removal between 95% and 99%. At equilibrium, only a specific amount of dye can be adsorbed by a specific adsorbent dosage. As the concentration increases, more adsorbent load will be needed to meet the high performance between 80% and 99%. This is associated with a small affinity towards malachite green dye by coconut shell activated carbon [18]. A rising trend is also depicted in Figure 7,

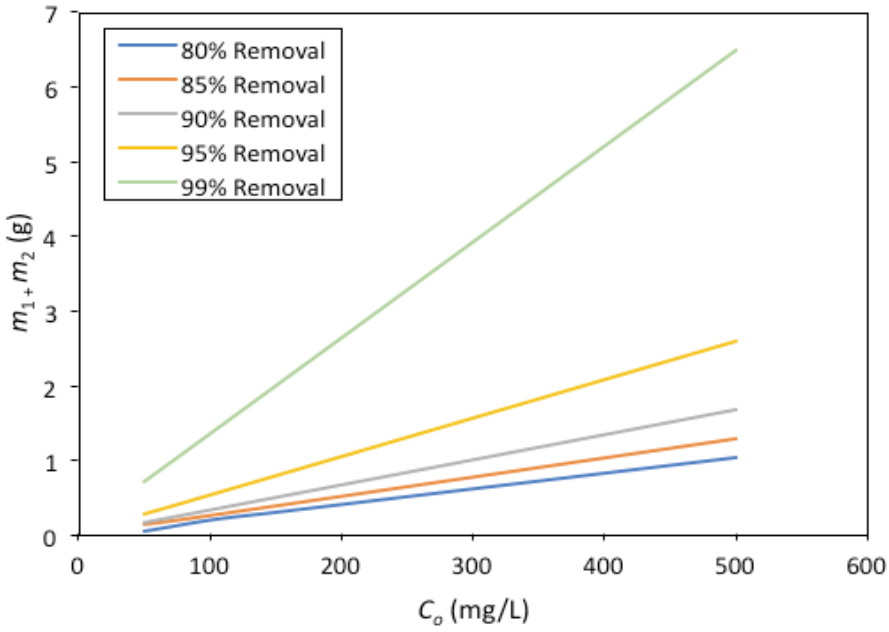

Figure 6 Effect of initial concentration on total adsorbent for different removal percentages

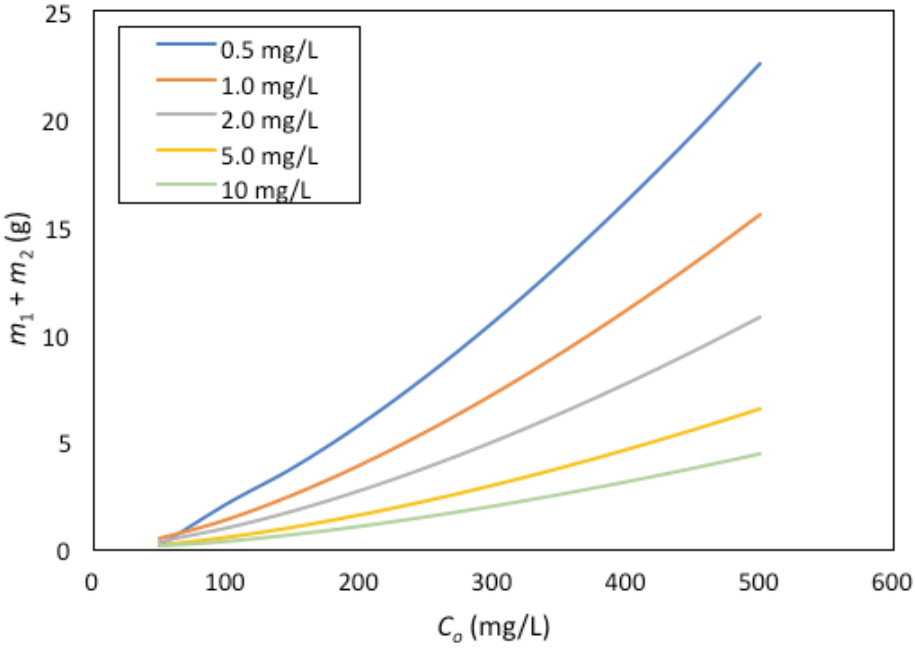

Figure 7 Effect of initial concentration on total adsorbent for different equilibrium concentrations

which underlines that a higher C_2 requires more adsorbent mass. Likewise, the total mass in the two-stage adsorber increases as C_o increases.

Figure 8 shows the capacity profiles at each stage for different removal percentages in the two-stage adsorber. The efficiency for dye removal in stage-2 is always lower than that in stage-1. This is due to the lower concentration of dye leaving stage-1 (C_1) and entering stage-2. Often, stage-2 is operating at low equilibrium in a two-stage adsorber.

Figure 9 presents the efficiency at stage-2 for different target C_2. The overall efficiency of adding a second stage in a two-stage adsorber is essentially constant at a given C_2 for any removal rates. However,

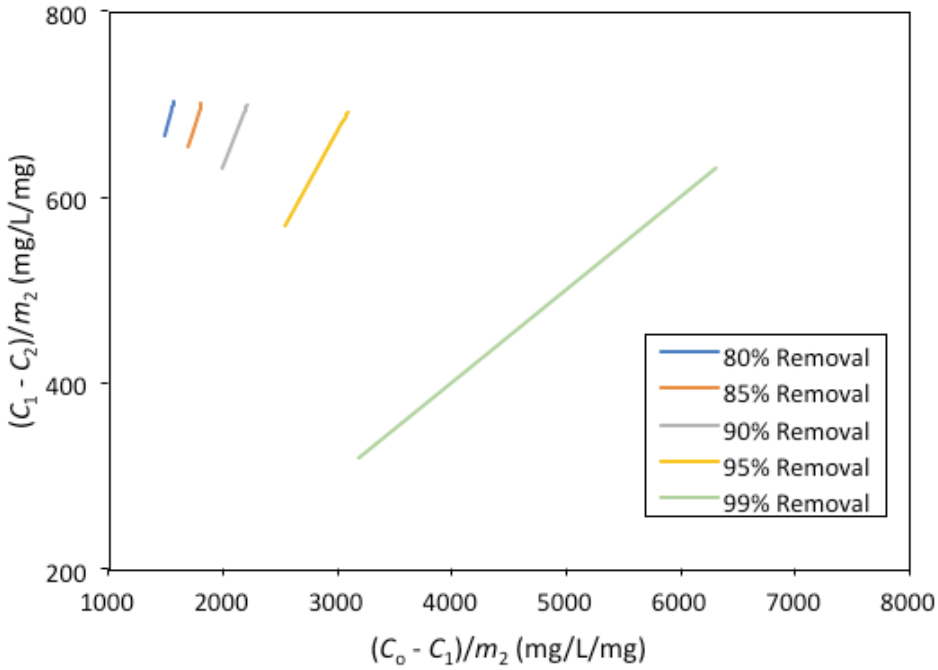

Figure 8 Capacity profiles in stage-1 and stage-2 at different removal percentages

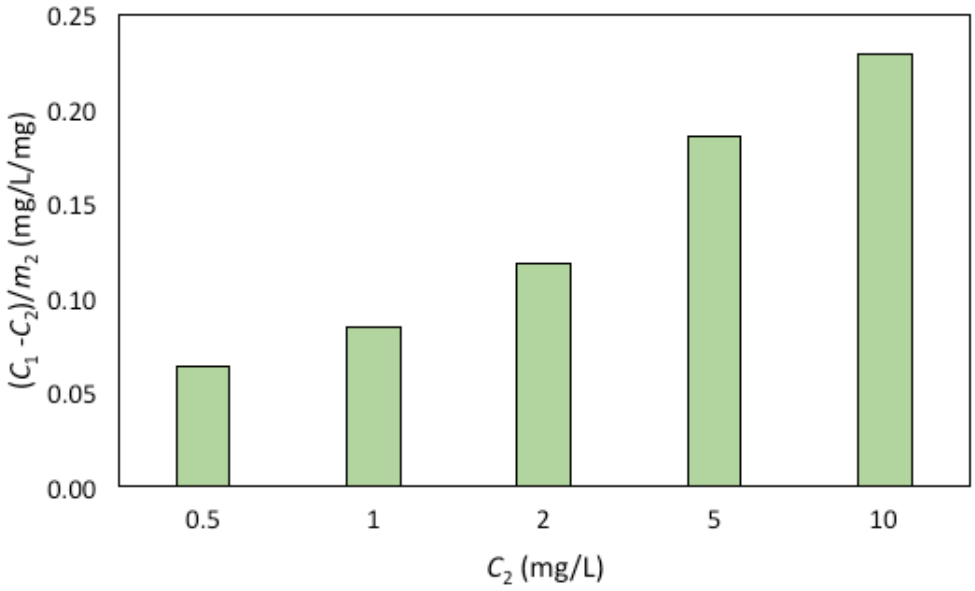

Figure 9 Capacity at stage-2 against C_2 in a two-stage adsorber

the efficiency in stage-2 increases as C_2 increases. Hence, the overall efficiency of a two-stage batch adsorption system can be observed to be significant in stage-2 at high targeted C_2.

The optimum mass was used to simulate the minimum contact time to accomplish the maximum adsorption of malachite green by coconut shell activated carbon. Figure 10 illustrates the profile of contact time against the adsorption system. The optimum contact time was also taken at sorption system 17, which gives a value of 1.43 min. According to [18], the time required to reach the equilibrium from 50 mg/L to 1.34 mg/L was 30 min in a single-stage adsorber. Therefore, the feasibility of a two-stage adsorber in minimizing the total contact time is significant because an additional unit of adsorber minimizes not only the total adsorbent mass but also

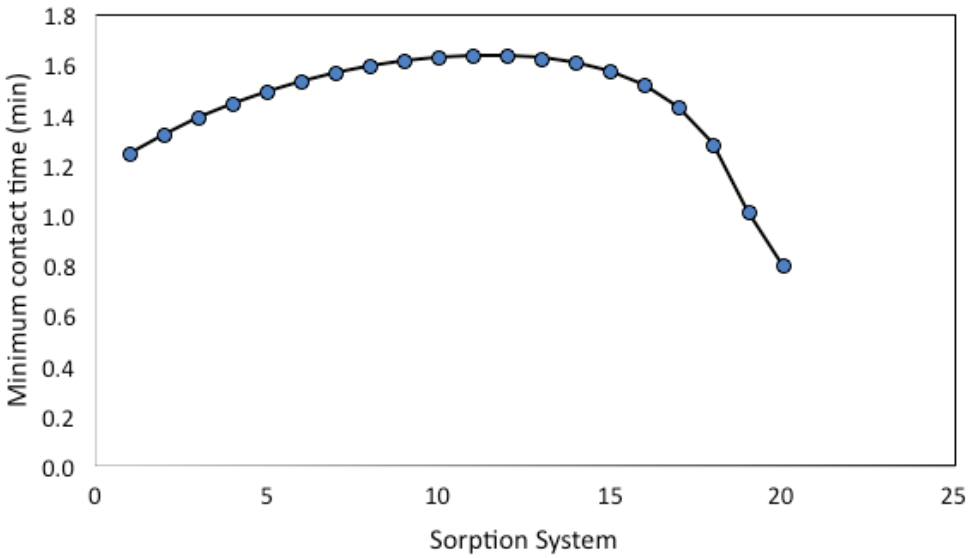

Figure 10 Minimum contact time for a two-stage adsorber

improves the economics and efficiency of dye removal.

CONCLUSION

A two-stage adsorber was numerically designed to predict the minimum mass of coconut shell activated carbon to achieve the desired malachite green removal at any effluent volumes at minimum contact time. The activated carbon mass was reduced by 22.4%, and the contact time was minimized from 30 min to 1.43 min to remove 50 mg/L dye. . Optimizing mass and contact time in a two-stage batch sorption system maximizes the use of adsorbent for overall efficiency and reduces operation costs. The performance evaluation at higher removal rates and lower equilibrium concentration allows the prediction of intermediate concentration and profiles of total mass for up-scaling purposes.

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