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# Malachite green adsorption by calcium-rich crab shell char via two-stage adsorber design

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**Abstract.** The present work was aimed to evaluate the optimum mass of crab shell biochar and adsorption contact time in a two-stage adsorber design for malachite green. The model was developed to predict optimum adsorbent mass and adsorption profiles at specified volumes and concentrations of dye effluent. Results show that the adsorbent mass can only be reduced by 1.91 % because of the adsorbent's strong affinity towards malachite green. Accordingly, the adsorption contact time to achieve equilibrium has dramatically reduced from 150 min to 31 min. In the performance evaluation, the adsorbent mass in stage-1 is always higher than that in stage-2 to subside the adsorbent load in achieving the target removal at optimum dosage. From the response surface methodology, the most significant parameters in two-stage adsorber design are adsorption time at stage-2 and malachite green concentration. The predicted values of adsorbent mass and time are essential in designing the cost-competitive two-stage adsorption process for industrial wastewater treatment.

**Keywords:** crab shell char; malachite green; two-stage adsorber; mass optimization; performance evaluation.

## 1. Introduction

Dyes are widely used in fabric and paper printing industries [**Error! Reference source not found.**]. Malachite green, methylene blue and Congo red are examples of dyes commonly used in regular basis. Dyes can find their ways into the water bodies because of lack of effluent handling and treatment. The presence of dye in lakes or rivers creates an unpleasant environment of colored waters that degrades the aesthetic nature and aquatic ecosystem. The release of dye effluent can lead to life-threatening illnesses such as kidney failure, damaged nervous system, skin irritation, rashes. Synthetic dyes are hard to remove as they are purportedly designed to resist biodegradation and fading under extreme conditions. Methods such as coagulation, membrane filtration, microorganism discoloring, reverse osmosis and adsorption are available to treat dye effluent [1, **Error! Reference source not found.**]. Of these, adsorption is preferred because the process is efficient, cheap and requires simple design and easy to scale-up [2-**Error! Reference source not found.**].

Owing to its cheap and sustainable source, biomass-derived carbon material has attracted increasing attention to be used in adsorption [**Error! Reference source not found.**-7]. Activated carbon has been widely used to treat organic and inorganic contaminants in water. However, the production cost is too expensive because the conventional feedstocks such as coal and petroleum pitch are not renewable. In addition, the quest for lignocellulosic wastes as potential substitute to activated carbon often hampered by further activation, oxidation, amination, which could compromise the feasibility for large scale production [7]. Biochar is a product from the direct pyrolysis of biomass which could be the right adsorbent candidate for dye adsorption. The effectiveness of biochar in adsorption is linked to its inherent physicochemical properties, including specific surface, surface functionalities, cation/anion exchange capacity and mineral content [**Error! Reference source not found.**]. Crustacean shell, a class of natural biomass is composed of highly mineralized chitin-protein fibers arranged in Bouligand pattern. Crustacean waste, such as crab shell contains 20-40 % proteins, 20-50 % calcite and 15-40 % chitin [**Error! Reference source not found.**]. Due to its high chitin content, it has been identified as a promising feedstock to produce engineered carbon materials [**Error! Reference source not found.**, **Error! Reference source not found.**]

One-stage batch adsorber is common in dye adsorption process. However, the adsorbent mass and adsorption profiles are not fully capitalized in achieving the desired performance at different effluent volumes and concentrations at industrial scale. For an economically viable process, two-stage adsorber has been proposed. In a two-stage adsorption, two consecutive batches are employed to attain the same equilibrium concentration or removal of the same effluent volume, wherein the dosage varies depending on the intermediate concentration leaving the stage-1 upon entering the stage-2. However, only limited application of such data has been directed towards the design of adsorption treatment system [**Error! Reference source not found.**-16]. Furthermore, the two-stage adsorber design for high-performance adsorbents is not widely documented in literature, so restricting their potential to be exploited for the

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wastewater treatment applications. In this work, we reported the theoretical optimum adsorbent mass and adsorption time, and the most significant parameter of two-stage adsorber of crab shell char for malachite green removal. The chemical-free synthesized adsorbent has displayed a tremendous capacity of malachite green in one-stage adsorber [17]. The simulation data were discussed to shed better understanding on the performance of two-stage adsorber of crab shell char towards sustainable wastewater treatment.

## 2. Experimental

### *2.1. Methods*

Dai et al. [17] reported an astonishing performance of malachite green removal by crab shell char. Table 1 shows the Langmuir and pseudo-second-order constants from [17]. The data were used as basis for two-stage adsorber simulation using Microsoft Excel.

**Table 1.** Adsorption constants for two-stage adsorber design [17].

| Langmuir model | | | Pseudo-second-order model | | |
|---|---|---|---|---|---|
| $q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $q_t$ (mg/g) | $k_2$ (g/mg.min) | $R^2$ |
| 12502 | 0.0906 | 0.920 | 11757 | $4.08\times10^{-6}$ | 0.909 |

The Langmuir equation is given as:

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \qquad (1)$$

where $q_e$ (mg/g) is the equilibrium capacity, $q_m$ (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 expressed as:

$$q_t = \frac{q_e{}^2 k_2 t}{1+q_e k_2 t} \qquad (2)$$

where $q_t$ (mg/g) is the capacity at any time, $t$ (min) and $k_2$ (g/mg·min) is the pseudo-second-order rate constant.

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

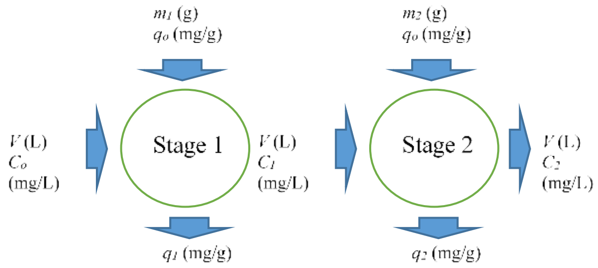


**Figure 1.** Schematic representation of two-stage adsorber (adapted from [15]).

In 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 $C_o$ (mg/L) to intermediate concentration $C_1$ (mg/L) in stage-1, and then to $C_2$ (mg/L) at equilibrium in the stage-2. The material balance for each stage can be written as:

$$V(C_0 - C_1) = m_1(q_1 - q_0) \qquad (3)$$

$$V(C_1 - C_2) = m_2(q_2 - q_0) \qquad (4)$$

The design objective was to treat 30 mL of malachite green solution at initial concentration, $C_o$ = 6584 mg/L. A series of equilibrium concentration, $C_1$ from 6584 mg/L to 350 mg/L [17] in a 300 mg/L step-size (sorption system number) was considered in stage-1 (sorption system 1, step-size = 0; sorption system 2, step-size = 300 mg/L, and so on). The volume, $V$ was varied between 30 mL and 250 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:

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

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

$$\frac{m_1+m_2}{V} = \frac{1}{q_m K_L}\left(\frac{(C_0-C_1)(1+K_L C_1)}{C_1} + \frac{(C_1-C_2)(1+K_L C_2)}{C_2}\right) \quad (7)$$

Equation (7) was differentiated against $C_1$, where $\frac{\mathrm{d}(m_1+m_2)/V}{\mathrm{d}C_1} = 0$ to give:

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

The optimum mass for each stage can be computed by Equations (7) and (8). Different removal rates (80% to 99%) and final concentrations (50 mg/L to 800 mg/L) at the discharge of stage-2 were set to evaluate the performance of 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:

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

The removal percentage, $R$ was determined as:

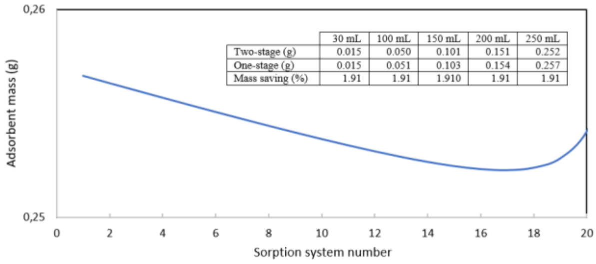
$$R = 100\left(\frac{C_o-C_2}{C_o}\right) \qquad (10)$$

The most significant parameter and confidence level in two-stage adsorber design were computed with the aid of Minitab 17 statistical software. A 2-level factorial design of response surface method was used to optimize the malachite green removal via two-stage adsorber.

Figure 2 shows the mass saving in two-stage adsorber for different effluent volumes treated. The mass of crab shell char increases as the volume of dye effluent increases to meet the removal performance [13, 14]. The mass increases from 0.015 g to 0.252 g for the increase in effluent volume from 30 mL to 250 mL. For all effluent volumes, the optimum mass was estimated at adsorption number 17. The variation in adsorbent mass between one-stage design and two-stage design becomes more prevalent as the volume increases in upscaling [16]. In two-stage adsorber, the adsorbent mass has been reduced by 1.91 %.

## 3. Results and discussion

Figure 2 shows the mass saving in two-stage adsorber for different effluent volumes treated. The mass of crab shell char increases as the volume of dye effluent increases to meet the removal performance [13, 14]. The mass increases from 0.015 g to 0.252 g for the increase in effluent volume from 30 mL to 250 mL. For all effluent volumes, the optimum mass was estimated at adsorption number 17.



| | 30 mL | 100 mL | 150 mL | 200 mL | 250 mL |
|---|---|---|---|---|---|
| Two-stage (g) | 0.015 | 0.050 | 0.101 | 0.151 | 0.252 |
| One-stage (g) | 0.015 | 0.051 | 0.103 | 0.154 | 0.257 |
| Mass saving (%) | 1.91 | 1.91 | 1.910 | 1.91 | 1.91 |

**Figure 2.** Profile of adsorbent mass to treat 250 mL effluent volume in a two-stage adsorber (Inset: Optimum mass for effluent volumes of 30 mL to 250 mL).

The variation in adsorbent mass between one-stage design and two-stage design becomes more prevalent as the volume increases in upscaling [16]. In two-stage adsorber, the adsorbent mass has been reduced by 1.91 %.

To treat 250 mL effluent, stage-1 adsorber requires 0.205 g biochar to decrease the concentration from 6584 mg/L to 1484 mg/L, while stage-2 needs 0.047 g biochar to accomplish the equilibrium at concentration of 350 mg/L. Thus, the total adsorbent mass required for two-stage adsorber is 0.252 g, that is lower than that of one-stage adsorber which consumes 0.257 g. At any volumes, the adsorbent mass is always bigger at stage-1 because the high concentration gradient is necessary to reduce the burden in stage-2 in attaining the equilibrium [15].

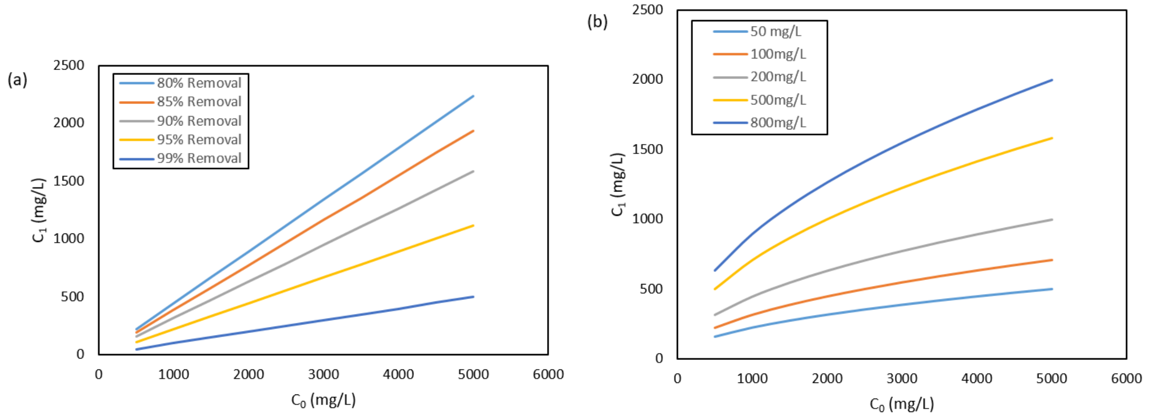


**Figure 3.** Intermediate concentration, $C_1$ against initial concentration, $C_o$ at different (a) adsorption performances and (b) targeted concentrations at stage-2, $C_2$.

Figure 3 explains the relationships between the intermediate concentration, $C_1$ and the initial concentration, $C_o$ at different performances and stage-2 concentrations, $C_2$. In Figure 3(a), the lines are linear for each desired performance. The gradient decreases in steepness as the performance rises to 99 %. Accordingly, $C_1$ is smaller at 99 % removal, and the magnitude increases as the percentage decreases. Similarly, $C_1$ is smaller at targeted $C_2$ = 50 mg/L, and the magnitude surges with increasing $C_2$. A small $C_1$ implies a more adsorbent mass to be consumed in stage-1 to bring the removal of dye in stage-2 at low equilibrium concentration [13, 15]. It highlights the effectiveness of two-stage batch adsorber design at industrial scale to meet the desired performance of highly concentrated dye effluent using crab shell char [14, 17, 18].

Figure 4 shows the relationships of adsorbent mass with initial concentration, $C_o$ for different removal performances and concentrations at stage-2 in a two-stage adsorber. The profiles were obtained at a fixed effluent volume of 30 mL. In Figure 4(a), the relationship is linearly proportional for the targeted removal percentages of malachite green. The higher the removal percentage, the more the mass of crab shell char would be needed to accomplish the separation [14, 16]. There is a huge leap from 95 % to 99 %, suggesting a higher adsorbent dosage necessary to surpass the mass transfer resistance in liquid phase in approaching the complete removal of dye in solution. An increasing pattern is also displayed in Figure 4(b). Likewise, the total adsorbent mass increases as $C_o$ increases.

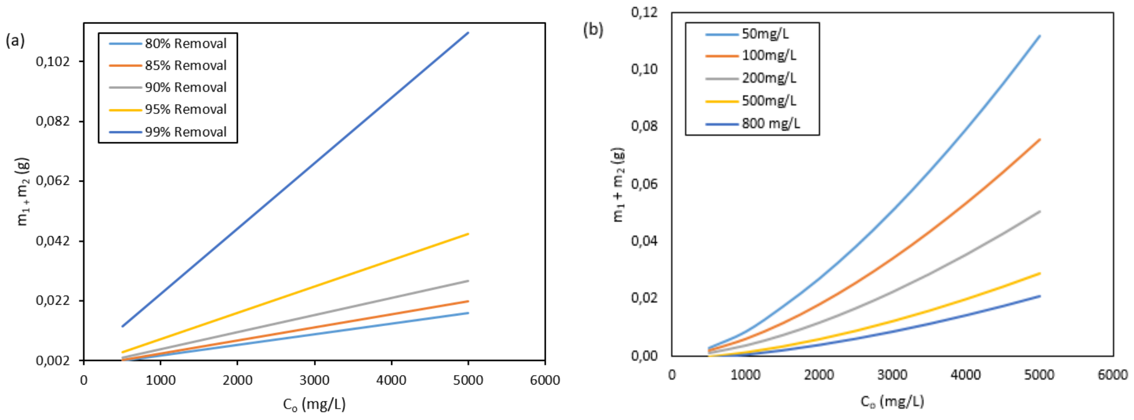


**Figure 4.** Adsorbent mass against initial concentration for different (a) removal performances and (b) concentrations at stage-2.

Figure 5(a) shows the capacity profiles at each stage for various removal performances. Obviously, the efficiency for dye removal in stage-2 is always lower than that in stage-1. This is due to the lower concentration of malachite green leaving stage-1 as intermediate concentration, $C_1$ and entering the stage-2 [13]. Often, stage-2 is running at low equilibrium. Figure 5(b) depicts the efficiency at stage-2 for different target $C_2$. The efficiency in stage-2, $(C_1\text{-}C_2)/m_2$, slightly increased with $C_2$ for any removal rates, suggesting that the overall efficiency is significant in stage-2 at high targeted $C_2$ [14].

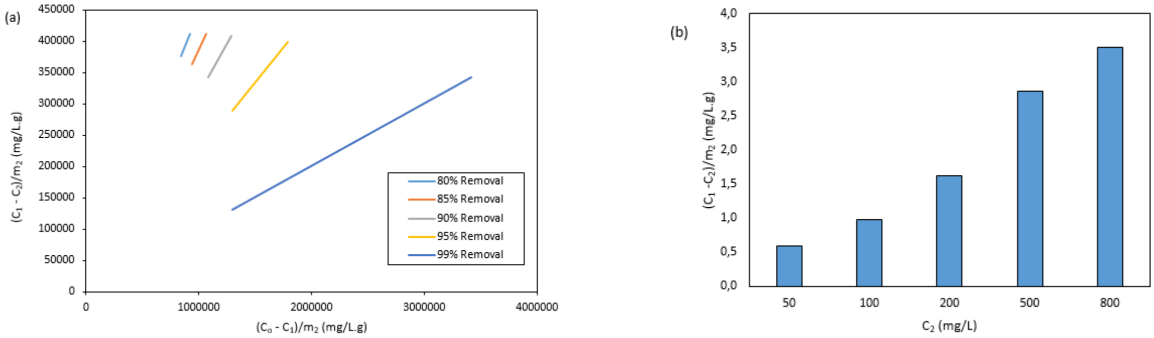


**Figure 5.** (a) Capacity profiles in stage-1 and stage-2 at different removal percentages and (b) efficiency at stage-2 against $C_2$.

The optimum mass was used to simulate the minimum contact time to accomplish the maximum adsorption of malachite green by crab shell char. According to Dai et al. [17], the time taken for one-stage adsorber of biochar to adsorb 11800 mg/g malachite green from 6000 mg/L dye concentration in 200 mL solution is 150 min. From Figure 6, the optimum adsorption time of 31 min was determined at sorption system 19. It exhibits a 79 % reduction in adsorption process as compared to one-stage adsorber. 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 improves the economics and efficiency of dye removal for industrial wastewater treatment [15, 16].

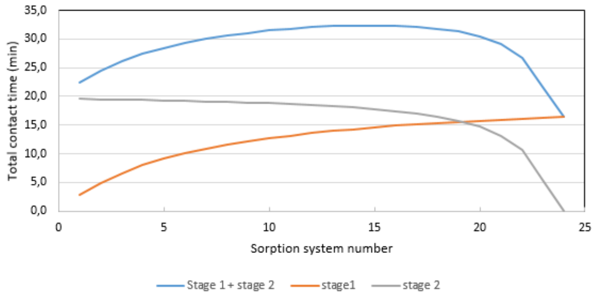
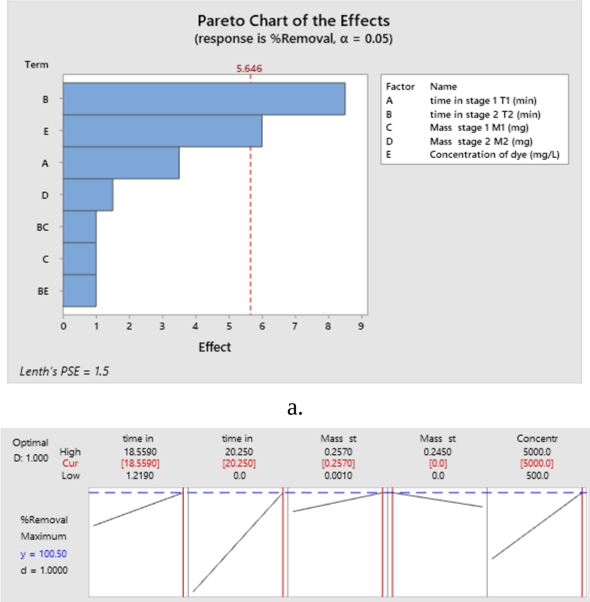


**Figure 6.** Adsorption contact time of malachite green by crab shell char in two-stage adsorber design.

Figure 7 shows the parametric effects by RSM. Any effects that extend beyond the reference line of the Pareto chart are significant. Therefore, the most significant parameters are contact time at stage-2 and malachite green dye concentration, as illustrated in Figure 7(a). This agrees with the analysis of variance, where the 2-way interaction of these parameters exhibits a p-value $< 0.05$. In Figure 7(b), the optimization plot reveals that, for a 250 mL effluent of malachite green dye with concentration of 5000 mg/L, the maximum predicted values of adsorbent mass and contact time for both stages are as follows: 0.257 g and 18.6 min for stage-1, and 0.001 g and 20.3 min for stage-2. This is in line with an earlier observation and prediction. When *d* value is unity, it statistically represents a 100 % removal efficiency. So, a 99 % malachite green adsorption was reached using a two-stage adsorber based on a 95% confidence level.



a.

b.

**Figure 7.** Parametric effects by RSM in two-stage adsorber of calcium-rich crab shell char for the treatment of 250 mL effluent containing 5000 mg/L malachite green, (a) Pareto chart and (b) optimization plot.

## 4. Conclusions

A two-stage adsorber was numerically designed to show the feasibility of using crab shell char for industrial-scale wastewater treatment of dye effluent. The dosage of biochar can be minimized to 1.91 % at any volumes of effluent because of the high affinity of adsorbent towards malachite green. Also, the total contact time can be optimized from 150 min to 31 min, that renders a 79 % time saving for operation. The 2-way interaction of contact time at stage-2 and malachite green concentration is the most significant parameter. The two-stage adsorber is advantageous in maximizing the adsorbent for overall efficiency and cost-competitive process, thus providing useful insights into the up-scaling for industrial wastewater treatment.

## Abbreviation

$C_o$: initial concentration; $C_e$: equilibrium concentration; $C_1$: concentration leaving stage-1 or intermediate concentration; $C_2$: concentration leaving stage-2 at equilibrium; $K_L$: Langmuir sorption affinity; $k_2$: pseudo-second-order rate constant; $m_1$: adsorbent mass entering stage-1; $m_2$: adsorbent mass entering stage-2; $q_o$: initial removal capacity; $q_e$: removal capacity at equilibrium; $q_m$: maximum removal capacity at surface saturation; $q_t$: removal capacity at any time; $q_1$: removal capacity at stage-1; $q_2$: removal capacity at stage-2; $t$: contact time; $V$: volume of reactor.

### *Availability of data and materials*

Data and simulation spreadsheet are available upon request.

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## Conflict of interest

Authors declare no conflict of interest.

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