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Response surface methodology and kinetic study for removal of colour and chemical oxygen demand from coffee wastewater by using spent coffee grounds

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ABSTRACT

Removal of chemical oxygen demand (COD) and colour from coffee wastewater using waste from industry are required due to abundant source for wastewater treatment. This paper presents a treatment of COD and colour from coffee wastewater by using spent coffee grounds (SCG) biochar. The removal of COD and colour was performed using a standard jar test procedure for the effect of pH, adsorbent dosage, and contact time. The samples for phosphoric acid (H_3PO_4) at the ratios of 1:2 (SCG: acid solution) was prepared for impregnation onto SCG. Afterwards, the samples were carbonized at 700°C in 1 h period. The results revealed that the optimum removal condition was obtained at the SCG biochar dosage of 20 g, pH 4 and in 60 min of contact times. The maximum colour and COD removal were approximately 99%. The isotherm model and adsorption kinetic model was conducted in the study. The selected data obtained were fitted using linear regression via Microsoft Excel. The regression analysis shows the adjusted R^2 obtained is above 90%, which indicates the best fitting data. The analysis of variance analysis proved that the mathematical expression could be used to predict the removal of colour and COD from coffee wastewater. Besides, response surface methodology is used to analyse the optimum parameters in colour and COD adsorption using SCG biochar to increase the adsorption efficiency further.

Keywords: Spent coffee ground; Biochar; Coffee wastewater; Colour removal; COD removal; Response surface methodology

1. Introduction

Recently, coffee culture is one of the global phenomena according to market research and the second highest consumed beverage, at more than 9 million tons annual consumption. Besides, approximately US$173 billion value the coffee industry in over 70 countries, making it a popular source of employment worldwide [1]. The rapid growth of the coffee market is due to innovation in types of brewed coffee beverage, online commercialisation and changes out of home consumption [2]. Due to the high production, coffee will end up generating an accumulation of waste.

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The total waste estimation is around 11.2 billion tons and roughly 2 tons per person [3], including coffee wastewater. According to [4], the by-product of coffee is a significant waste that cannot be removed quickly from the coffee wastewater. Coffee wastewater is a severe environmental problem, especially the colour due to contaminants contain tannins. Coffee effluent contains a high amount of dark brown pigment and characterized as a high chemical oxygen demand (COD). Even a small amount of colour and COD concentration discharge can affect aquatic life due to the blocked sun rays causing interference with the photosynthesis process occurring in the river. Even though there are no latest cases this year about coffee wastewater, each company needs to treat the wastewater based on the Environmental Quality (Industrial Effluent) Regulations 2009 to ensure the overall contamination is reduced to the acceptable specification. Hence, appropriate treatment of disposal can avoid water pollution and sustain human health.

Nowadays, coagulation and flocculation are the most popular method for the wastewater treatment. In general, this method is the most effective in removing the suspended solids, but the colour remains. Hence, to fill the gap, new alternatives have been introduced: the electrochemical advanced oxidation process (EAOPs) using boron-doped diamond (BDD) electrodes to remove the dark brown colour of coffee. However, this method incurs high operating and capital costs. Cost-effective ways have been found in the treatment of coffee wastewater using affordable coagulation technology, which is *Moringa oleifera* seed extract (MOSE). However, MOSE is not effective in reducing COD and colour, especially when it is low [5].

Hence, to overcome the problem, activated carbon adsorption process has mainly been used as the low-cost adsorbent for agricultural waste. Thus, the treatment system using spent coffee grounds (SCG) biochar has been introduced to overcome the problem in wastewater treatment performance. The SCGs are prevalent in the adsorption of gaseous molecules due to its porous surface structure properties, affordability and potential as a source for biochar carbon [6].

Thus, this method aimed at removing the colour effectively and reducing the COD of coffee wastewater to comply with Environment Quality (Industrial Effluent) Regulation 2009 in terms of removal colour and COD. According to [7], SCG biochar as adsorbents can achieve high percentage removal of colour and COD.

However, fewer studies have been conducted on optimization of this treatment process due to limitation such as adsorption efficiency. Therefore, some significant controls are necessary for the treatment process to achieve maximum removal of colour and COD. Linear regression is a statistical method used to prove the reliability of the treatment process by generating a mathematical equation related to the expected value of a response. This method has been implemented mostly in the chemical industry and other fields such as physical, engineering, biological and others [8].

Next, response surface methodology (RSM) is used to analyse the optimum parameters in colour and COD adsorption using SCG biochar to increase the adsorption efficiency further. RSM can be expressed as a popular analytical tool in any optimization process. The function of RSM is to design the experiments, construct the experiment model, estimate the effect of the parameters, and examine the optimum conditions to achieve the desired response [9,10]. RSM can simultaneously optimize several variables, which can lower the number of experimental runs [9–14]. Thus, it can reduce the time consumed in trial work, cost of operation, as well as capable of achieving optimum condition after simulating the relationship between parameters including initial pH of wastewater, SCG dosage, the contact time of SCG and others.

This research aims to carry out the experimental study of parameters affecting the colour and COD removal from actual coffee wastewater using SCG biochar as an adsorbent. This study's parameters were the effect of the SCG biochar dosage, initial pH of wastewater, and contact time of SCG biochar on the performance of colour and COD removal. This study then conducted the isotherm model and adsorption kinetic model using the achieved adsorption data to identify the best fitting of the SCG biochar.

This study also performed a linear regression to develop a mathematical model to indicate the removal process as well as to compare the effectiveness of each treatment method for colour and COD removal. Lastly, RSM was used as an analytical tool for the optimization process in this study to examine the optimum conditions to achieve the desired response.

2. Methodology

2.1. Material

The materials used in this research were actual coffee wastewater and coffee beans waste collected from the coffee industry in Penang. The SCG biochar were prepared by impregnated using an activation agent was 14.6 M phosphoric acid (H_3PO_4) that was purchased from Merck (Malaysia).

2.2. Analysis instruments

The instruments used to characterize the pH of wastewater in this study were handheld water resistance pH meter (HANNA HI-8424). Meanwhile, to describe the concentration of colour and COD inside wastewater, the instruments used were HACH DR6000 UV-Vis Spectrophotometer and HACH DRB200 and HACH DR6000, respectively.

2.3. Experimental procedure

2.3.1. Industrial wastewater characterization and sampling

20 L the actual wastewater collected from the source of discharge at a coffee company. Then, the wastewater was characterized for pH, colour, and COD of the solution.

2.3.2. Actual coffee wastewater

The prepared wastewater model was characterized for pH, colour, and COD concentration. Real coffee wastewater was collected and stored in the freezer at 6°C before its use for the experiments.

2.3.3. Spent coffee ground preparation

The SCG biochar were produced by adapting the methodology described by previous studies [7]. The precursor (SCG) was initially washed with distilled water, dried at 105°C for 24 h, cooled down to room temperature, and sieved at 300 µm. For chemical activation, SCG was weighed (100 g) and impregnated with 14.6 M phosphoric acid (H_3PO_4) at the mass ratios 1:2 (SCG: acid solution) Afterwards, the samples were sonicated for 1 h, dried at 105°C for 24 h, cooled down to room temperature. In this study, the SCG powder was carbonized at 700°C in the porcelain crucible using 1700C Muffle Furnace (ALARGE). Once the selected temperature was reached, the samples were kept in the furnace for 1 h. At the end of the process, the samples were cooled down to room temperature (20°C).

The activated carbon samples were initially washed with distilled water until its pH was neutral in focusing ash removal. The samples were dried at 105°C for 4 h and washed with 1 M of hydrochloric acid (HCl) to ensure that the excess of dehydrating agents was eliminated. The ratio used was 1:2 (SCG: acid solution) for 20 min using a magnetic stirrer hot plate (IKAMAG). Afterwards, the samples were dried at 105°C for 24 h, cooled down to room temperature.

2.3.4. Adsorption experiments

Adsorption batch tests were adapted from previous studies using 200 mL of coffee wastewater. Blanks containing only coffee wastewater and no adsorbent were also assessed. An orbital shaker was used to keep the samples constantly agitated at 125 rpm. To determine the interference of the adsorbent dose (3, 4, 5, 10, 15, and 20 g), pH (1, 2, 4, and 7), and contact time of adsorbents (30–180 min with 30 min of increment) by agitation for the colour and COD removal from coffee wastewater.

The influence of various operating parameters were studied by keeping others constant using the optimum parameter adapted from [7] and varying one parameter. In the first parameter, the adsorption process using SCG biochar conducted by adjusting the dosage SCG biochar at 3, 4, 5, 10, 15, and 20 g. The process was agitated continuously at 125 rpm using an orbital shaker. The selection of SCG biochar dosage was based on a previous study [7]. The initial pH of coffee wastewater was kept constant for each different dosage at pH 4 and 180 min of contact times [7].

The optimum dosage can be obtained from the highest removal of colour and the COD after-treatment process. In the second parameter, the adsorption process using SCG biochar was operated similarly to the first parameter. The influence of various operating parameters was studied by keeping others constant using the optimum parameter from and varying one parameter [7]. However, the initial pH differed at 1, 2, 4, and 7. The dosage of SCG biochar was kept constant based on the optimum conditions obtained from the first parameter experiment. In the third parameter, the adsorption process using SCG biochar was operated similarly to the first and second parameters but with differ of contact time. The contact time was between 30 to 180 min, with 30 min of increment. The dosage of SCG biochar and the initial pH was kept constant based on optimum condition obtained from the experiment in the first and second parameter.

2.3.5. Analysis of adsorption results

The adsorption capacity of SCG was determined using Eq. (1):

$$Q_e = \frac{\left(C_i - C_e\right)V}{m} \tag{1}$$

where Q_e = equilibrium adsorption capacity (mg/g), V = volume of coffee wastewater (L), m = mass of adsorbent (g).

The adsorption isotherm was a mechanism study that involved the interaction between the SCG biochar and the colour and COD of coffee wastewater in the equilibrium state. Commonly Langmuir and Freundlich isotherm was applied for colour and COD adsorption models. The Langmuir isotherm is shown in Eq. (2) while Freundlich isotherm is shown in Eq. (3),

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

where Q_e = equilibrium adsorption capacity (mg/g), Q_m = equilibrium capacity for complete monolayer adsorption (mg/g), K_L = adsorption equilibrium constant (L/mg).

$$Q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

where K_F and n were Freundlich constants.

The adsorption process can be more effective by performing adsorption kinetics studies. The adsorption kinetics model described on the adsorption mechanism and the rate-limiting steps that affect the adsorption rate. Thus, to examine the adsorption of colour and COD by varying the contact time, the pseudo-first-order and pseudo-second-order kinetic models were used. The kinetic models are shown in Eqs. (4) and (5),

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where q_t = equilibrium adsorption capacity (mg/g) at time t (min), k_1 = pseudo-first-order kinetic rate constant (min^{-1}), k_2 = pseudo-second-order kinetic rate constant (min^{-1}).

The graph of $\log(q_e - q_t)$ against t and t/q_t against t was plotted. Thus, the rate constant k_1 and k_2 can be obtained by computing the slope of the curve and value of the y-intercept, respectively.

2.3.6. Statistical analysis of colour and COD removal by linear regression

The linear regression consists of two types, which are simple linear and multiple linear. The linear regression is conducted to develop a regression model by considering the adsorption experiment's data. Choosing independent and dependent variables in a linear model is done using wastewater factor. The removal percentage of colour and COD was selected as the dependent variable. Meanwhile, the dosage of SCG biochar, initial pH and contact time of adsorbent were chosen as independent variables. The general equation proposed for regression modelling is formulated in Eq. (6),

$$Y_n = aX_n + bX_n^2 + c \quad (6)$$

where Y_n = Colour and COD removal percentage (%), X_n was SCG dosage, initial pH, and contact time.

2.3.7. Response surface methodology

RSM can be expressed as a popular analytical tool in any optimization process. The function of RSM is to design the experiments, construct the research model, estimate the effect of the parameters, and examine the optimum conditions to achieve the desired response [9,10]. Besides, RSM can optimize several variables simultaneously at one time, which can lower the number of experimental runs [9–14].

3. Results and discussion

3.1. Characterization of coffee wastewater

The characterization of effluent from the coffee industry is carried out according to Standard Methods for the Examination of Water and Wastewater [15]. Based on Table 1, the parameter value for a colour, COD, and pH was listed.

3.2. Effect of the SCG biochar dosage on colour and COD removal

The dosage of SCG biochar significantly affected in removing the efficiency of colour and COD as well as the adsorption capacity by consuming a specified dosage. Thus, the 200 mL of coffee wastewater at an initial pH with 180 min at 125 rpm agitation speed was selected as an adsorption condition. The effect of SCG biochar was carried out by varying the amount of SCG biochar at 3, 4, 5, 10, 15, and 20 g. Therefore, the percentage removal in colour and COD is plotted against SCG biochar dosage and adsorption capacity of colour and COD against the SCG biochar dosage. As a result, the optimum SCG biochar dosage for the highest removal of colour and COD was achieved.

Table 1
Initial parameter values for the characterization of coffee wastewater

Parameter	Initial values
pH	2.00
Colour	12,500 ADMI
COD	58,300 mg/L

Based on Fig. 1, the percentage of colour and COD removal rises slowly at 4 g of dosage from the initial dosage of SCG biochar. Then, the colour and COD removal increase drastically at 10 g of SCG biochar dose. The percentage removal for both colour and COD rises again at 20 g doses of SCG biochar in the range of 94%–99%. The fluctuations in the percentage COD removal can be verified by [16]. The justification of this crisis was about the optimum impregnation ratio in the preparation of SCG biochar. Besides, it was challenging to find out the optimum impregnation ratio due to their ash contents.

Based on Fig. 2, the adsorption capacity for both colour and COD was increase in the order of SCG biochar dosage of 3 and 4 g. The adsorption capacity of colour and COD are developed when the SCG biochar are added from 5 to 20 g. However, there is a slight drop from 4 to 5 g, which only affect COD adsorption capacity. According to [17], the reduction of adsorption could be attributed to the precipitation or the chelation with different active adsorbent binding sites.

The relationship between the percentage removal and adsorption capacity for both colour and COD against the SCG biochar dosage are similar due to the same trend shown in the plotted graph in Figs. 1 and 2, respectively. The general intention in an increment of percentage removal and adsorption capacity of colour and COD were the increase of adsorption sites and surface areas. As the SCG biochar dosage are increased, the accessibility of the sorption surface

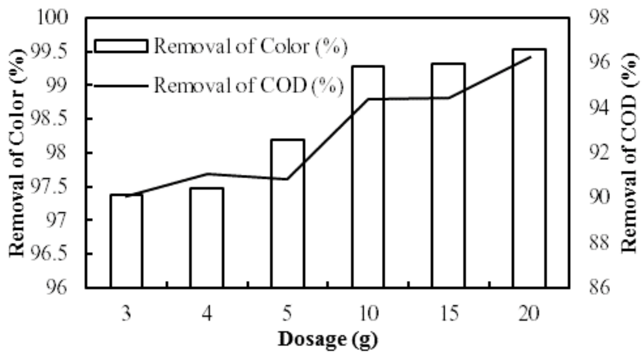

Fig. 1. Effect of SCG biochar on adsorption capacity.

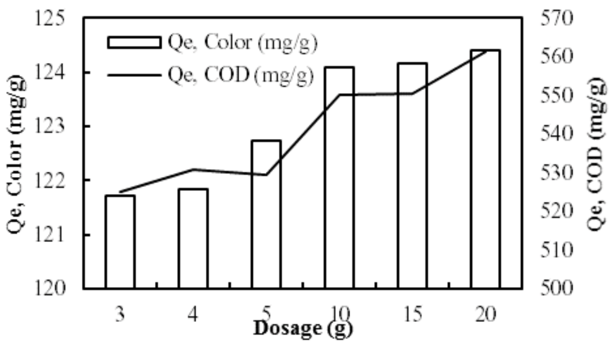

Fig. 2. Effect of SCG biochar on adsorption capacity.

and the adsorption sites also increases, which leads to more adsorbate attached to the surface. Furthermore, the maximum percentage removal of colour and COD are 99.5% and 96.2%, while the maximum adsorption capacity for colour and COD are 124.4 and 561.1 mg/g, respectively. The final dosage of SCG biochar is 20 g for both parameters. Hence, the optimum dose for wastewater treatment is at 20 g of SCG biochar, which similar performance in the previous study [7]. Therefore, the dosage for experiments of other parameters was carried out at 20 g of SCG biochar as an optimum dosage due to the highest removal for both colour and COD.

3.3. Effect of pH of the solution for colour and COD removal

The efficiency of the colour and COD removal are strongly dependent on the pH of the initial coffee wastewater. In this parameter study, the amount of 20 g of SCG biochar is added into varies the initial pH of the coffee wastewater with pH 1, 2, 4, and 7 and contact time of 180 min. The 0.1 M hydrochloric acid (HCl) is used to adjust the initial pH of coffee wastewater from pH 2 to pH 1. Meanwhile, the pH higher than pH 2 was adjusted using 0.1 M sodium hydroxide (NaOH). Therefore, the graph of percentage removal in colour and COD is plotted with the adsorption capacity of colour and COD against the initial pH of initial coffee wastewater in Figs. 3 and 4. Thus, the optimum pH of initial coffee wastewater for colour and COD removal can be succeeded.

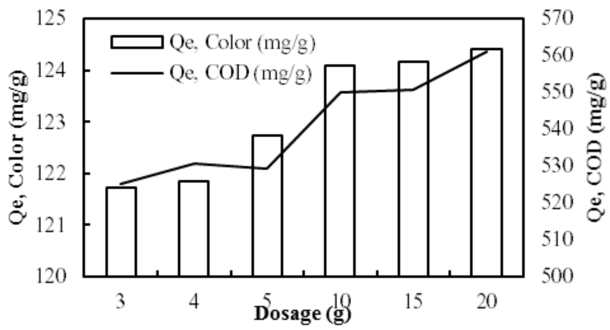

Fig. 3. Effect of initial pH of coffee wastewater on colour and COD removal.

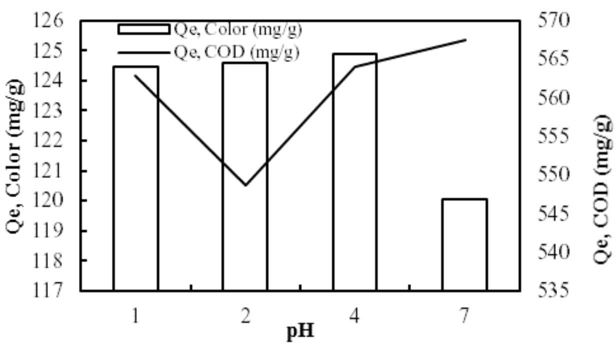

Fig. 4. Effect of initial pH of coffee wastewater on adsorption capacity.

Referring to Fig. 4, the altered pH from the initial pH of 2 to pH 1 is justified by the competitive adsorption between aqueous H^+ ions and COD on the surface sites of SCG biochar lower pH. The surface of the SCG biochar may accumulate a positive charge, which can absorb lignin and tannin's negative charges [18]. Thus, the percentage removal of COD is highest at pH 1 compared to pH 2, from 96.5% to 94.1%. According to [7], the percentage removal of colour and COD increased from pH 2 to pH 4 and reached the most considerable removal around pH 4–6. At the neutral pH conditions, pH 7, the percentage of COD removal remained nearly constant.

Meanwhile, the percentage removal of colour at the neutral pH conditions follows a decreasing trend. These circumstances are verified as the adsorption of colour and COD in coffee wastewater are favourable at acidic conditions compared to alkaline conditions. Therefore, the percentage of removal, colour and COD rise gradually at pH 2 and pH 4 from 99.6% to 99.9% and 94.1% to 96.8%, respectively. The decline of percentage colour removal at pH 7 is due to the competition between OH^- of NaOH and tannin would occur. This interaction resulted in a lower percentage of colour removal. However, the percentage of COD removal increases due to the neutral active sites on the lignin's adsorbent surface. The most significant percentage removal of colour and COD is at pH 4. Therefore, it is selected as the optimum pH.

Based on Fig. 4, as the pH increases, the colour and COD adsorption capacity also increase at pH 2 and pH 4 from 124.6 mg/g to 124.9 and 548.63 to 564.1, respectively. However, at pH 7, the adsorption capacity of colour sharply declines, but slowly increases for colour adsorption capacity. These conditions caused by the excess of OH^- ions at the adsorption sites produce a repulsion force towards organic molecules and colour cations. Thus, the functional groups on the adsorbent surface become negatively charged and reduce the adsorption capacity.

Hence, it can be concluded that the optimum pH suitable for colour and COD removal was in the pH range from 2 to 4. In this study, the optimum pH is achieved at pH 4. According to [7], this result specifies that the SCG biochar most probably exhibited neutral surface charges at acidic pH instead of alkaline pH. Moreover, the chemical activation of SCG biochar using H_3PO_4 reduces the content of hemicellulose, lignin, and cellulose crystallinity so that the specific surface area will increase [19]. Thus, the adsorption capacity for colour and COD removal is higher using the SCG biochar at optimum pH. As a result, the pH in the next experiment's parameter is carried at 20 g of SCG biochar and pH 4 due to maximum removal efficiency for both colour and COD.

3.4. Effect of the contact time on colour and COD removal

Contact time is also one of the essential parameters to be controlled so that the usage of 20 g SCG biochar and the initial pH of coffee wastewater at pH 4 were completely efficient in removing the colour and COD. The contact time was carried out from 30 to 180 min with 30 min of increment. Optimum contact time is needed to define the time required for the colour and COD to reach equilibrium conditions after contact with SCG biochar. Thus, the graph of percentage removal and adsorption capacity for colour and COD is plotted in Figs. 5 and 6. The trend for both graphs are observed, and both have similar patterns.

Based on Fig. 5, the percentage removal for colour and COD rise from 30 to 60 min. As expected, as an increase of removal percentage, the contact time also increases until the reach at equilibrium state between the amount of adsorbate on the SCG biochar and the remaining coffee wastewater. The maximum percentage of COD removal is 97.4%, with contact time of 60 min.

Meanwhile, the highest percentage of colour removal is 99.9% in 90 min. The percentage removal of colour and COD within 60 min is defined as an active phase due to a large number of active sites. The next stage is described as a slower adsorption process, which causes smaller colour and COD percentage removal. Thus, the equilibrium point is labelled in 60 min, and generally, the adsorption sites are already saturated to the maximum uptake capacity [7].

However, the curve of percentage removal of colour and COD started to fluctuate rapidly after reaching the equilibrium point. The result obtained proved that SCG biochar is not suitable for colour and COD percentage removal after 60 min. The slower adsorption during the increasing contact time might be due to the lower rate of solute diffusion into the adsorbent pores [20]. From the accomplished study, the highest removal of percentage colour and COD efficiency are 99.8% and 97.4%, followed by the lowest percentage removal of colour and COD at 99.4% and 97.1%, respectively.

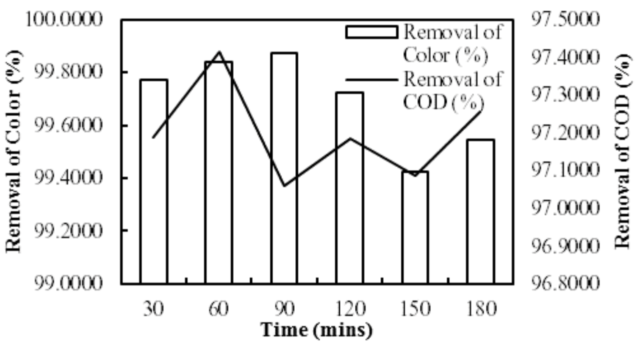

Fig. 5. Effect of contact time on colour and COD removal using SCG biochar.

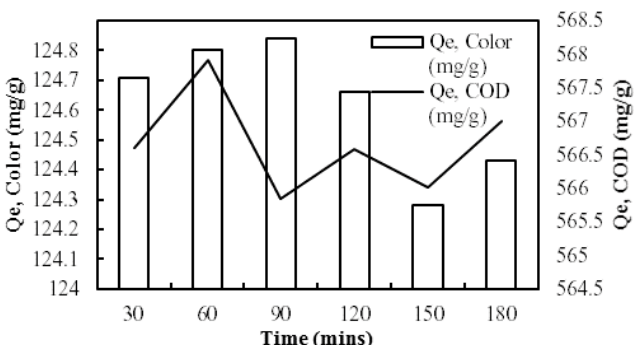

Fig. 6. Effect of contact time on adsorption capacity using SCG biochar.

The adsorption capacity for colour and COD in this study obtained a similar trend with the percentage removal of colour and COD as shown in Fig. 6.

From 30 min to 60 min, the adsorption capacity for colour and COD are 124.7–124.8 and 566.6–567.9, respectively. Based on Fig. 6, the highest of the adsorption capacity for both colour and COD reach 60 min before the trend started to fluctuate from 90 min to 150 min. The higher adsorption capacity of colour and COD are due to higher active sites on the SCG biochar testified by [21]. At this stage, the percentage removal could accelerate an external diffusion, and surface adsorption occurs due to more vacant active adsorption sites [22,23].

Hence, the trend shows that most adsorption happens on the surface rather than the pore of SCG biochar [24]. As the time increases, the SCG biochar surface decreases due to the higher amount of colour and COD which inhibited the SCG biochar surface vacant site availability. Thus, the adsorption process becomes slow [25]. The researcher also described that the lower adsorption capacity is caused by a lack of sufficient surface area to hold the colour and COD in the coffee wastewater.

Therefore, the optimum contact times in 60 min with 20 g of SCG biochar and initial pH 4 are used in isotherm and kinetic study due to the maximum removal efficiency for both colour and COD.

3.5. Adsorption isotherm

The most commonly applied adsorption models are Langmuir and Freundlich isotherm. Figs. 7 and 8 describe the plot of Langmuir isotherm for adsorption of COD and colour by using SCG biochar. The adsorption process follows the linear form of the Langmuir equation illustrated in Eq. (7).

The constant Q_m and K_L were obtained from the slope and intercepts of the plot between C_e/Q_e vs. C_e.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (7)$$

where Q_e = equilibrium adsorption capacity (mg/g), Q_m = maximum capacity for complete monolayer adsorption

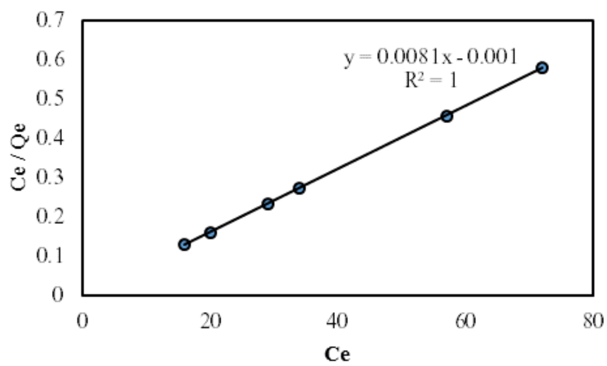

Fig. 7. Langmuir isotherm model for COD adsorption onto the SCG biochar.

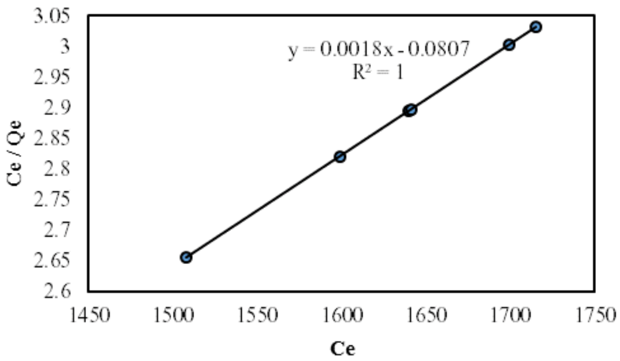

Fig. 8. Langmuir isotherm model for colour adsorption onto the SCG biochar.

(mg/g), K_L = Langmuir adsorption equilibrium constant (L/mg), C_f = concentration of colour or COD at equilibrium (ADMI or mg/L).

Table 2 shows the summarised findings from the plot of Langmuir isotherm. The value of R_L indicated the type of Langmuir isotherm to be irreversible (R_L = 0), linear (R_L = 1), unfavourable (R_L > 1), or favourable (0 < R_L < 1). The R_L values between 0 and 1 indicate favourable adsorption. The R_L values for both colour and COD adsorption obtained between 0 and 1, thus both adsorption onto SCG biochar are favourable.

Table 2 shows that the *R*-squared values obtained for both colour and COD adsorption are 1. Thus, it specifies that the data is well fitted with Langmuir isotherm. According to [26], if the *R*-square value obtained is more than 0.7, the value is considered as a firm effect size typically. Besides, the maximum adsorption capacities, $Q_{\max}$ of the SCG biochar are in colour and COD adsorption. According to [27], as the adsorption energy is high, the K_L resulted in the high affinity of the SCG biochar with the *R*-squared values and $Q_{\max}$ values.

Freundlich isotherm model describes the heterogeneous and capacity of adsorption related to the concentration of colour and COD at equilibrium. The adsorption process followed the linear form of the Freundlich equation illustrated in Eq. (8). The data obtained from the contact parameter is also fitted into the Freundlich isotherm model and plotted for colour and COD adsorption using SCG biochar, as shown in Figs. 9 and 10. The constant *n* and K_F were obtained from the slope and intercepts of the plot between $\ln Q_e$ vs. $\ln C_e$.

$$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (8)$$

where K_F = Freundlich constants, $1/n$ = heterogeneity factor.

Table 3 shows the summarised results from the Freundlich isotherm plot.

Figs. 9 and 10 show a straight-line plot of $\ln Q_e$ against $\ln C_e$, which performed the Freundlich isotherm model for both colour and COD adsorption. Based on Figs. 9 and 10, the *R*-squared values obtained from the Freundlich isotherm are 0.96 and 0.99 for colour and COD, respectively. The *R*-squared values are near to 1, which follow the isotherm well. According to [26], if the *R*-square value obtained is more than 0.7, the value is considered to be a firm effect size typically.

Based on the Langmuir isotherm and Freundlich isotherm data, it proved that the best description of the adsorption process was Langmuir isotherm compared to the Freundlich isotherm. The *R*-squared values explained that Langmuir isotherm's data is a better fit to the Langmuir isotherm model. Based on linear regression values, the correlation of the Langmuir isotherm model for both colour and COD were R^2 = 1 is higher compared to the correlation coefficient of Freundlich isotherm model R^2 = 0.9606 and 0.9995, respectively. Therefore, it represented that the SCG biochar had similar binding sites equally active with monolayer coverage [28].

3.6. Adsorption kinetics model

The pseudo-first-order and pseudo-second-order kinetic models are used to examine the adsorption of colour and

Table 2
Langmuir isotherm parameter for colour and COD adsorption onto SCG biochar

Isotherm parameter	Langmuir isotherm for colour adsorption	Langmuir isotherm for COD adsorption
$Q_{\max}$ (mg/g)	123.4568	555.5556
K_L (L/mg), (1/ADMI)	8.1000/ADMI	0.0223 L/mg
R_L	0.1×10^{-3}	0.0747
R^2	1	1

Table 3
Freundlich isotherm parameter for colour and COD adsorption onto SCG biochar

Isotherm parameter	Freundlich isotherm for colour adsorption	Freundlich isotherm for COD adsorption
K_F (L/mg), (1/ADMI)	8.1670/ADMI	17.1930 L/mg
N	–333.333	–35.2113
R^2	0.9606	0.9995

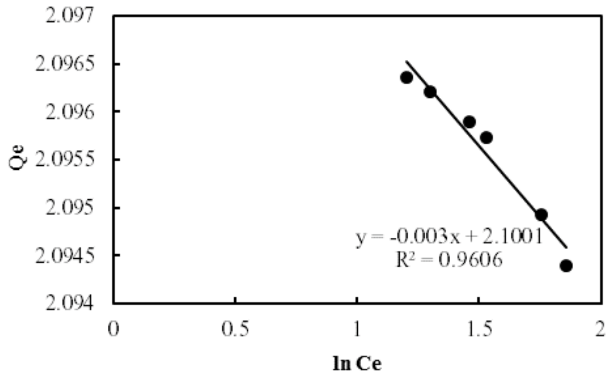

Fig. 9. Freundlich isotherm model for colour adsorption onto SCG biochar.

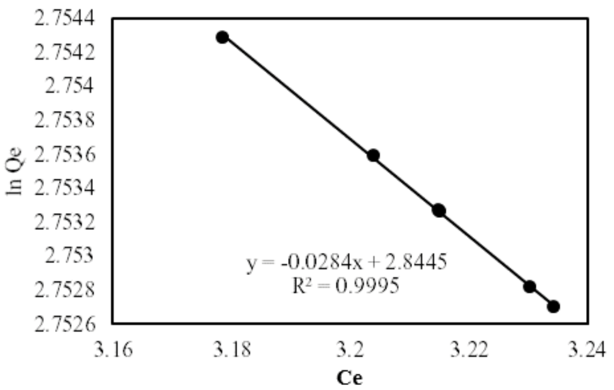

Fig. 10. Freundlich isotherm model for COD adsorption onto SCG biochar.

COD by varying the contact time. The pseudo-first-order model is mostly used for the adsorption of solute from liquid solutions [29]. Thus, the straight-line forms for colour and COD adsorption onto SCG biochar are illustrated in Figs. 11 and 12, respectively, using Eq. (9).

$$\log\left(Q_e - Q_t\right) = \log Q_e - \frac{k_1}{2.303}t \tag{9}$$

where Q_t = equilibrium adsorption capacity (mg/g) at time t (min), k_1 = pseudo-first-order kinetic rate constant (min^{-1}).

Figs. 11 and 12 were plotted t against $\log(Q_e - Q_t)$, which a linear relation for the pseudo-first-order kinetic model. The kinetic parameters for colour and COD

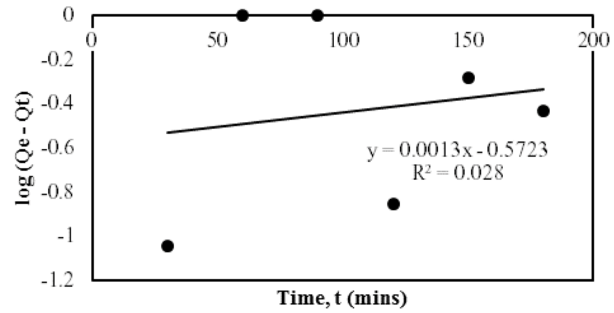

Fig. 11. Pseudo-first-order kinetic model for colour adsorption onto SCG biochar.

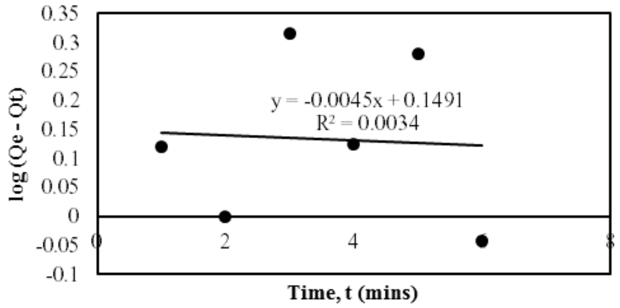

Fig. 12. Pseudo-first-order kinetic model for COD adsorption onto SCG biochar.

adsorption onto SCG biochar are shown in Table 4. The value of k_1 (slope) and Q_e (y-intercept) indicating the rate constant of the adsorption and amount of colour, and COD adsorbed are shown in Table 4.

The straight-line forms for colour and COD adsorption onto SCG biochar as demonstrated in Figs. 13 and 14, respectively. Both graphs are plotted t/q_t against t, a linear relation for the pseudo-second-order kinetic model using Eq. (10). The value of k_2 (slope) and Q_e (y-intercept) indicating the rate constant of the adsorption and amount of colour and COD adsorbed are shown in Table 5.

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{10}$$

where Q_t = equilibrium adsorption capacity (mg/g) at time t (min), k_2 = pseudo-second-order kinetic rate constant (min^{-1}).

Therefore, based on the low correlation coefficient, R^2 obtained in the pseudo-first-order models for colour

Table 4
Pseudo-first-order kinetic model parameter for colour and COD adsorption onto SCG biochar

Kinetics parameter	Pseudo-first-order kinetic model for colour adsorption	Pseudo-first-order kinetic model for COD adsorption
k_1 (min^{-1})	2.9940×10^{-3}	0.0104
Q_e	0.2677	1.4096
R^2	0.028	0.0034

and COD adsorption are 0.028 and 0.0034. Thus, it proved that the model failed in providing an accurate model fit for the experimental results. Meanwhile, for the correlation coefficient, R^2 of pseudo-second-order is equal to 1 for both colour and COD adsorption. Hence, it confirms that pseudo-second-order models for colour and COD are an excellent correlation on adsorption of SCG biochar. As a result, the graphs plotted for pseudo-second-order fit well with high linearity compared to pseudo-first-order. According to [26], the R^2 value lesser than 0.3 is considered a feeble effect of size.

3.7. Linear regression analysis on colour and COD removal

The results of regression statistics for percentage removal of colour and COD for variables dosage of SCG biochar

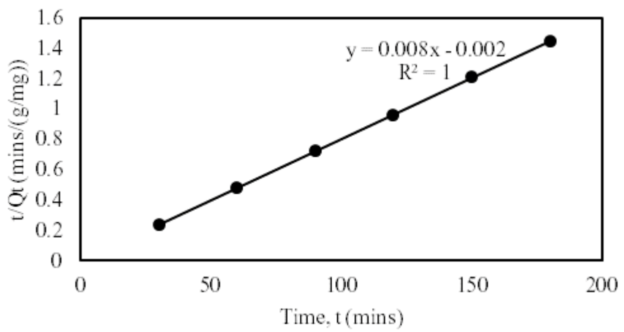

Fig. 13. Pseudo-second-order kinetic model for colour adsorption onto SCG biochar.

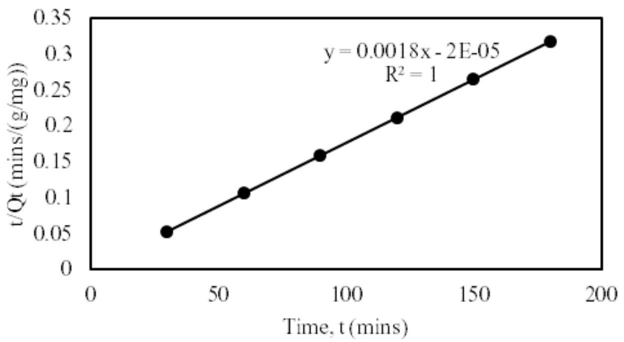

Fig. 14. Pseudo-second-order kinetic model for COD adsorption onto SCG biochar.

Table 5
Pseudo-second-order kinetic model parameter for colour and COD adsorption onto SCG biochar

Kinetics parameter	Pseudo-second-order kinetic model	
	Colour adsorption	COD adsorption
k_2 (min^{-1})	–0.032	–0.1620
Q_e	125	555.5556
R^2	1	1

adsorbent, initial pH of the solution, and the contact time of adsorbent are shown in Table 6. Based on Table 6, the value of the adjusted R^2 for the multiple regression of the percentage removal of colour for the variable dosage of SCG biochar adsorbent, and initial pH of the solution are 0.93242 and 0.95697, respectively. For the adsorbent's contact time, the simple linear regression is used according to the software's suggestion. Hence, the value of the R^2 is 0.48224. The data for variable, the dosage of SCG biochar adsorbent and initial pH of the solution are considered as fit since the values approach almost to 1. Still, only the data for a contact time of adsorbent do not fit well. All the R^2 values present the predictor variables, which correlate to the percentage removal of colour by 93.242%, 95.697%, and 48.224%.

Furthermore, the percentage removal of COD is only dependent on the dosage of SCG biochar adsorbent. For the initial pH of the solution and the contact time of adsorbent, the percentage COD removal were insignificant. The regression is concluded to be unreliable due to insignificant value of R-square and adjusted R-square.

Thus, the value of the adjusted R^2 for the multiple regression of the percentage removal of colour for variables dosage of SCG biochar adsorbent is 0.91968. Since the adjusted R^2 value almost approach 1, the data obtained fitted well. Hence, the predicator variables correlated to the percentage removal COD is 91.968%.

Therefore, it can be concluded that the coefficient determination for percentage removal of colour has a stronger relationship between independent and dependent variables since most of the variables approaching 1 for adjusted R^2 values in this study.

Table 7 shows analysis of variance (ANOVA) for percentage removal of colour and COD for each variable. Greater F-value and small P-value indicates great significance of the corresponding coefficient.

Table 6
Regression statistic for percentage removal of colour and COD for each of the variables

Regression statistic		
Parameters	Percentage removal of colour	Percentage removal of COD
Dosage of spent coffee grounds (SCG) biochar		
Multiple R	0.979	0.976
R-square	0.959	0.952
Adjusted R-square	0.932	0.919
Initial pH of the solution		
Multiple R	0.993	–
R-square	0.986	–
Adjusted R-square	0.957	–
Contact time of spent coffee grounds (SCG) biochar		
Multiple R	0.765	–
R-square	0.586	–
Adjusted R-square	0.482	–

Table 7
ANOVA analysis for percentage removal of colour and COD in each of variable

Parameters		dF	Significant F	
			Colour removal (%)	COD removal (%)
Dosage of SCG biochar	Regression	2	0.008	0.011
	Residual	3		
	Total	5		
Initial pH of solution	Regression	2	0.119	–
	Residual	1		
	Total	3		
Contact time of SCG biochar	Regression	1	0.076	–
	Residual	4		
	Total	5		

The coefficients model and the coefficient colour and COD percentage removal in terms of each variable are illustrated in Table 8. The reliability of a significant coefficient can be determined from the *P*-value.

If the *P*-value is less than 0.05, the probability of the regression output is not obtained by random chance or null hypothesis. For the *P*-value higher than 0.05 means the regression output is obtained by random chance or null hypothesis. It also defines as a little or not significant. Based on Table 8, the regression for percentage removal of colour in terms of dosage, pH solution and contact time is less than 0.05.

Meanwhile, the *P*-values for percentage removal of COD in term of the dosage of SCG biochar adsorbent are more significant than 0.05. However, the *P*-values for the intercept are less than 0.05. Thus, a small percent of the probability of these regression outputs may be obtained by random chance or null hypothesis. Perhaps some of the outputs are considered as significant, whilst the rest can be described as slightly significant.

As a result, the regression output can be performed in the mathematical model equation. The equations are constructed according to Table 6. The multiple linear regression modelling for percentage removal of colour is done using Eqs. (11)–(13).

$$Y_1 = -0.012\ X_1^2 + 0.408\ X_1 + 96.25 \quad (11)$$

$$Y_1 = -0.224\ X_1^2 + 1.238\ X_1 + 98.39 \quad (12)$$

$$Y_1 = -0.002\ X_1 + 99.95 \quad (13)$$

The most significant variable in percentage removal of colour is the dosage of SCG biochar adsorbent. Still, other variables are slightly significant to the percentage removal of colour since not all of the coefficient's approach are less than 0.05. Then, the multiple linear models for percentage removal of COD in terms of SCG biochar adsorbent dosage is determined using Eq. (14). This effect also slightly significant to the percentage removal of COD.

$$Y_2 = -0.015\ X_1^2 + 0.684\ X_1 + 88.23 \quad (14)$$

Therefore, it can be concluded that the most significant percentage of colour removal is the SCG biochar adsorbent dosage. The mathematical model for percentage removal of colour is considered to the percentage of COD due to the SCG biochar as a natural adsorbent may also have slight contribution to the COD level in coffee wastewater. Therefore, SCG biochar seem more effective in removing the colour of coffee wastewater. However, the SCG biochar can still counter both colour and COD parameters but comprise a limitation in COD levels to achieve the permissible limit specified by IER2009.

Table 8
The model parameter for percentage removal of colour and COD in each variable

Parameters		Coefficient		P-value	
		Colour removal (%)	COD removal (%)	Colour removal (%)	COD removal (%)
Dosage of SCG biochar	Intercept	96.257	88.232	$1.3E^{-07}$	$3.6E^{-06}$
	X_1	0.408	0.684	0.018	0.068
	X_2	–0.012	–0.015	0.047	0.263
Initial pH of solution	Intercept	98.390	–	0.004	–
	X_1	1.238	–	0.210	–
	X_2	–0.224	–	0.143	–
Contact time of SCG biochar	Intercept	99.950	–	$1.2E^{-11}$	–
	X_1	–0.002	–	0.076	–

From the statistical results obtained, the models from Eqs. (11)–(14) are suitable in predicting the percentage removal of colour and COD within the selected experimental range variables. Besides, the experimental and predicted model values with different operating factors are provided in Table 9. The predicted values for percentage removal for colour and COD for each of the variables are closest to their experimental values due to their predicted R^2 values more than 0.05. Most of the values approached almost to 1. Besides, the percentage error below 1% means that the value is close to the experimental values. Since the evaluated percentage error is below 1%, it can be concluded that all the regression models fit well in predicting the percentage removal of colour and COD. The calculation for percentage error, as illustrated are following.

The plotted graph for actual and predicted vs. experimental of percentage removal of colour and COD are shown in Figs. 15–18 to observe the performance model.

3.8. Response surface methodology

A three-level three-factor Box–Behnken design is used to predict the optimal conditions for colour and COD adsorption by using SCG biochar as a function of several parameters like adsorbent dose, initial pH, and contact time via Table 10. The percentage of colour and COD removal plots for the three variables are predicted based on the model.

3.8.1. Combined effect of pH solution and adsorbent dosage at constant contact time

From Fig. 19, the three-dimensional plot shows the adsorbent dosage and pH of the solution significantly affect the percentage removal of colour. As the percentage removal of colour increases, the dosage of adsorbent increases proportionally for the entire range of pH values used in this study. Consequently, the maximum percentage removal of colour at pH 4, as demonstrated in the 3D plot. This can be clarified that the neutral surface charge of SCG biochar at acidic pH rather than at alkaline pH. According to [30], the surface of SCG biochar are mostly negative at alkaline pH. Thus, the SCG biochar will potentially repel the tannins groups relating to the colour of coffee wastewater. At lower pH, the attraction by the protonated surface of SCG biochar is minimal.

Moreover, the percentage removal is 98.91% at pH 1 when the adsorbent dosage is 3 g. The percentage removal of colour increases to 99.02 at pH 4 with the same amount of adsorbent dosage of SCG biochar. The percentage removal of colour is reduced at higher pH due to the repulsion between the OH^- ions and the SCG biochar surface negatively charged [31].

The dosage of SCG biochar adsorbent does not affect the percentage of colour removal at high pH. However, as the dosage of SCG biochar increases, the percentage of the colour removal increase with the pH until pH 4. Hence, this proves that the dosage of SCG biochar also significantly affects the percentage of colour removal when pH is increased. According to [32], as the adsorbent surface area and the adsorption sites increase, the adsorbent's dosage increases in achieving a higher percentage of colour removal.

Concisely, it can be concluded that the combined effect is more significant at the two factors, which are the pH of the solution and the adsorbent dosage. The percentage removal of colour increased as any of the factors increased.

3.8.2. Combined effect of contact time and adsorbent dosage at a constant pH of the solution

The combined effect of contact time and the adsorbent dosage is shown in Fig. 20 when the solution's pH is

Table 9
The experimental and predicted model values for different operating factors

Parameters	Removal of colour (%)		Error (%)	Removal of COD (%)		Error (%)
	Actual	Predicted		Actual	Predicted	
Dosage of spent coffee grounds (SCG) biochar	97.368	97.531	0.18	90.061	90.440	0.42
	97.469	97.843		91.033	91.004	
	98.189	98.131		90.799	91.538	
	99.272	99.211		94.368	93.758	
	99.325	99.691		94.437	95.228	
	99.528	99.571		96.250	95.948	
Initial pH of solution	99.571	99.528	0.04	–	–	–
	99.667	100.09				
	99.917	99.882				
	96.024	96.204				
Contact time of spent coffee grounds (SCG) biochar	99.770	99.890	0.12	–	–	–
	99.840	99.830				
	99.875	99.770				
	99.725	99.710				
	99.424	99.650				
	99.544	99.590				

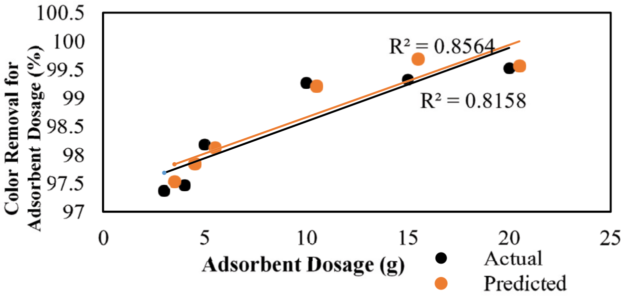

Fig. 15. Plotted graph for actual and predicted vs. adsorbent dosage for removal of colour.

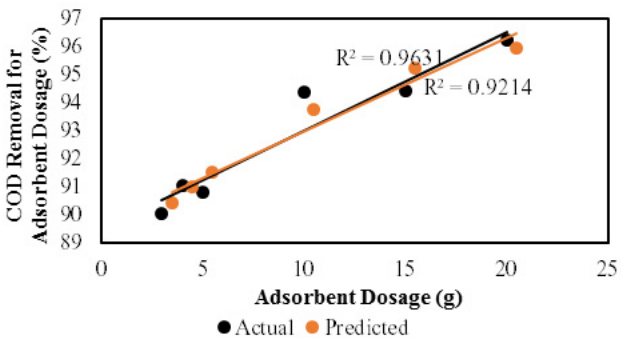

Fig. 16. Plotted graph for actual and predicted vs. adsorbent dosage for removal of COD.

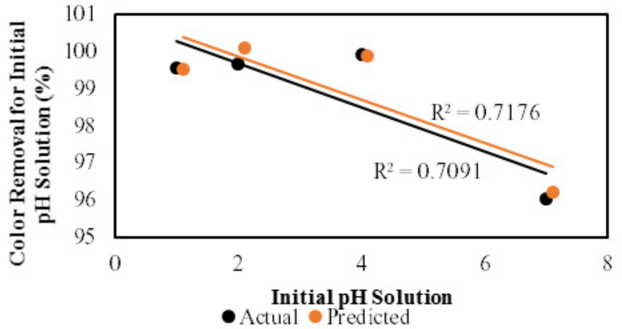

Fig. 17. Plotted graph for actual and predicted vs. initial pH of solution for removal of colour.

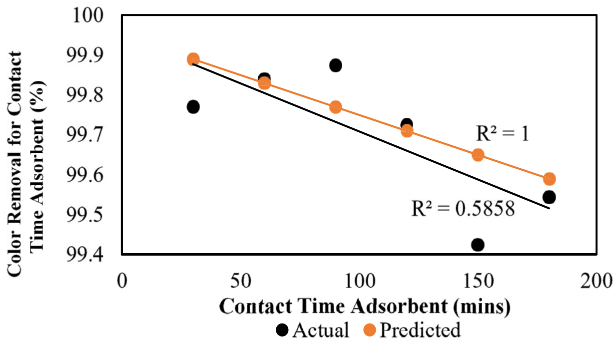

Fig. 18. Plotted graph for actual and predicted vs. contact time adsorbent for removal of colour.

observed from the three-dimensional plot. It is found that at a lower amount of SCG biochar, the contact time is invalid. However, at the higher amount of SCG biochar, the contact time changes have been sufficient for the percentage removal of colour. Thus, the percentage removal of colour is significantly affected by the dosage adsorbent of SCG biochar at any contact time. The steeper the gradient of the SCG biochar dosage, the higher the percentage removal of colour [33].

The percentage of colour removal does not rise with the increment of the adsorbent's contact time at any dosage of the SCG biochar adsorbent. It can be explained

Table 10
Results of the response by each experimental run suggested by RSM

Standard order	Run order	Factorial design	Blocks	Dosage (g)	pH	Contact time (min)	Colour removal (%)
1	1	2	1	3.0	1	105	98.91
2	2	2	1	20.0	1	105	99.63
3	3	2	1	3.0	7	105	97.73
4	4	2	1	20.0	7	105	98.45
5	5	2	1	3.0	4	30	99.02
6	6	2	1	20.0	4	30	99.74
7	7	2	1	3.0	4	180	98.94
8	8	2	1	20.0	4	180	99.66
9	9	2	1	11.5	1	30	99.54
10	10	2	1	11.5	7	30	98.36
11	11	2	1	11.5	1	180	99.47
12	12	2	1	11.5	7	180	98.28
13	13	0	1	11.5	4	105	99.67
14	14	0	1	11.5	4	105	99.67
15	15	0	1	11.5	4	105	99.67

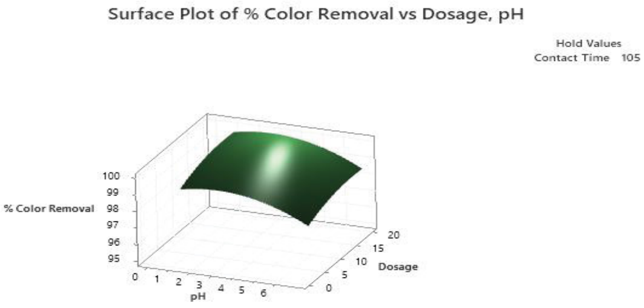

Fig. 19. Three dimensional plotted of the adsorbent dosage and initial pH of the solution at constant contact time.

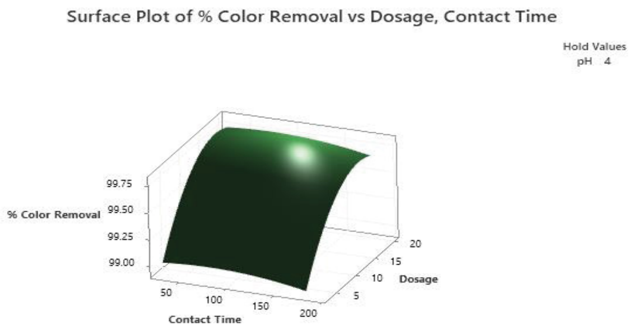

Fig. 20. Three dimensional plotted of the adsorbent dosage and contact time at constant initial pH of the solution.

that the adsorbent has reached the maximum adsorption capacity within 1 h. Thus, the surface area of the adsorbent is significantly low [7]. The adsorbent surface coverage has reached the maximum adsorption capacity within 1 h. Therefore, it can be concluded that the percentage of colour removal is independent of the adsorbent's contact time between 1 to 24 h.

3.8.3. Combined effect of contact time and pH of the solution at a constant adsorbent dosage

Fig. 21 shows the effect of contact time of adsorbent and pH of the solution on the percentage removal of colour at constant adsorbent dosage. It is observed that the percentage removal of colour increases by increasing the pH solution until pH 4. The percentage of removal drops after pH 4 due to the SCG biochar was exhibit neutral surface charges at acidic pH rather than alkaline pH, as explained earlier [7].

From Fig. 21 it is observed that the percentage removal of colour does not increase as the contact time of adsorbent increases. The percentage of the colour removal is almost the same for the contact time at 60, 120 and 180 min at pH 7. Thus, it could be chiefly due to the saturation of the adsorption capacity of the adsorbent after 60 min of contact time.

As a summary, the colour removal percentage is highly dependent on the solution's pH but independent on the contact time of adsorbent between 30 to 180 min.

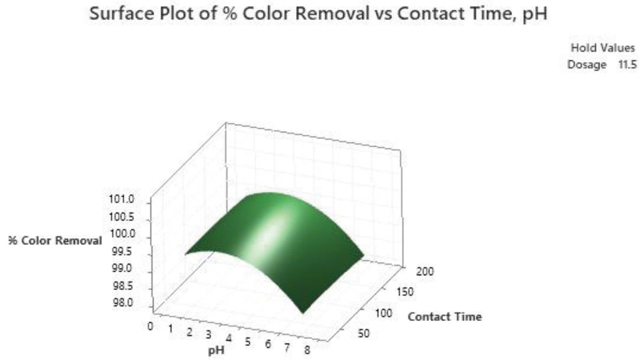

Fig. 21. Three dimensional plotted of the contact time and initial pH of the solution at a constant adsorbent dosage.

4. Conclusion

This study has established that SCG is suitable as an adsorbent in removing the colour and COD in coffee wastewater. However, there is a limitation in removing the COD in coffee wastewater to achieve the permissible limit specified by IER2009. In this study, the COD level of coffee wastewater is too high since it is taken from the coffee industry. Perhaps the number of chemical activation agents used in producing these SCG biochar are not enough to counter the COD level of this coffee wastewater. Moreover, both removals of colour and COD efficiencies are extensively influenced by three parameters during the adsorption test. Therefore, the highest percentage removal for colour and COD achieved are 99.84% and 97.19% with adsorption capacity at 124.8 and 567.92 mg/g adsorbent, respectively. On the other hand, the obtained result specifies that the maximum removal of colour and COD succeed at 20 g dosage of SCG biochar adsorbent, initial pH of the solution at 4, and 60 min of adsorbent contact time. Thus, to reach the result in the best accuracy, good agreement has been done by repeating the experiment with the gotten optimum conditions.

This study also conducted the isotherm and kinetic modelling. Thus, the best describes the adsorption mechanism of SCG biochar are Langmuir and Freundlich Isotherm, which specify the monolayer adsorption of colour and COD on the surface of SCG biochar adsorbent. The high correlation coefficient value based on the data plot of adsorption capacity for both colour and COD against contact time is on the pseudo-second-order kinetic model. Therefore, this model symbolised the adsorption kinetics of SCG biochar due to their R-value approach to 1.

Then, the mathematical expression corresponding with the data fitting by linear regression also has been conducted using Excel software. The mathematical expression for colour and COD percentage removal is performed with the interaction of SCG biochar adsorbent dosage, initial pH of the solution, and adsorbent contact time. The percentage removal colour and COD prediction have been made by the ANOVA analysis of mathematical expression using Excel software. The regression analysis established a model to represent the experimental data. The model is analysed to be significant with an *F*-value of less than the 0.05 and coefficient correlation, R^2 approach to 1.

Furthermore, the optimization study on the percentage removal of colour and COD accomplished by using RSM via Minitab software based on the regression analysis. The percentage removal of colour and COD in terms of SCG biochar adsorbent dosage, initial pH of the solution, and contact time of adsorbent have been presented in the 3D surface plot through prediction from the model. Therefore, the most significant percentage removal of colour achieved is 99% at the optimum conditions with 20 g dosage of SCG biochar, initial pH of the solution at 4, and 60 min of adsorbent contact time.

In short, a lot of pollution hazards are appearing due to the increase in production of spent coffee grounds discharged to the environment. Despite, SCG's contribution to pollution, coffee wastewater also causes pollution if the wastewater is not treated correctly. Thus, as an alternative, using SCG as an adsorbent can remove the colour and COD of coffee wastewater and reduce pollution.

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