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# Adsorption of methylene blue by kapok fiber treated by sodium chlorite optimized with response surface methodology

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ABSTRACT

Cationic dye methylene blue (MB) was removed from aqueous solution by kapok fiber treated with sodium chlorite ($NaClO_2$). During the treatment process of the adsorbent, response surface methodology (RSM) based on three-level three-factorial Box–Behnken design was used. The effects of three variables, such as $NaClO_2$ content (0.3–1.2 g), acetic acid (HAc) content (0.1–1.9 mL) and reaction temperature (60–90 °C) on the adsorption capacity for MB (as response) were examined. The optimum treatment conditions ($NaClO_2$ of 0.93 g, HAc of 1.42 mL and reaction temperature of 90 °C) were determined by the results of statistical analysis, under which an adsorbent was prepared and used to remove MB from aqueous solution. The effects of contact time, pH on adsorption and adsorption mechanism were investigated. The predicted value of model (105.48 mg/g) was in excellent accordance with experimental value (110.13 mg/g). The adsorption process was rapid and obeyed pseudo-second-order kinetics. The adsorbent showed excellent reusability with 0.1 mol/L of hydrochloric acid solution as desorbing agent and could be used as a potential adsorbent for cationic dyes containing wastewater treatment.



## 1. Introduction

Many dyeing industries give rise to dye-bearing effluents in the production processes and these problematic wastewaters have to be treated to accord with discharge limit before discharge not only for their high chemical and biological oxygen demand but also for suspended solids of toxic properties to aquatic life and reduce in light penetration. Most of these dyes are synthetic and exhibit complex aromatic structure, thus being stable and difficult to be biodegraded. Several techniques have been developed to treat dye effluents such as microbial degradation, chemical oxidation, membrane separation, bioaccumulation, electrochemical treatment, adsorption and reverse osmosis [1], and among these techniques, adsorption is generally preferred due to easy handling, high efficiency, low energy input and availability of different adsorbents [2,3].

The most commonly used adsorbent for dye removal was activated carbon, while difficult regeneration and high cost limited its wide application [4]. Currently, the removal of dyes using low-cost abundantly available adsorbents, such as sand [5], sepiolite [6], orange peel [7], banana peel [7] and pistachio hull waste [8] was attempted to search for appropriate adsorbents. However, the limited adsorption capacity or little mention of regeneration limited further application. Nowadays, new adsorbents with superior properties such as economy, simple regeneration and easy availability have been developed for dyes removal. The kapok fiber is a single-cell natural cellulose fiber, with 64% cellulose, 13% lignin, 8.6% water, 1.4–3.5% ash, 4.7–9.7% water-soluble substances, 2.3–2.5% xylan and 0.8% waxes [9,10]. The kapok fiber exhibits a rather thin cell wall with a huge hollow lumen full of air, and thus exhibits a low density, high bulkiness, good oil absorptivity and water-repellent nature [9,11]. Water cannot easily penetrate into the lumen for the presence of negative capillary entry pressure due to the large contact angle (>90°) between water and kapok fiber wall, and the large surface tension against air in the lumen [12]. Furthermore, waxy cutin on the kapok fiber surface makes it water repellent notwithstanding it is mainly composed of cellulose [13,14]. Compared to cotton fiber, the kapok fiber exhibits a lower content of cellulose and a higher content of lignin. Owing to its special properties mentioned above, kapok fiber is widely employed as stuffing for bedding, upholstery, life preservers and other water-safety equipment and for insulation against sound and heat [12]. It was reported that the cellulose and lignin can remove dyes from aqueous solution [15,16]. However, the interaction between lignin, other non-celluloses and cellulose makes part of hydroxyl groups in the cellulose not available to dye molecules, thus leading to decrease in amorphous part of cellulose, hydrophobic property and low dyeing efficiency of kapok fiber [17]. Therefore kapok fiber has not been investigated to the same extent as for other agro-products for its adsorption characteristics for dyes and few well-documented

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published literatures only by Chinese researchers on its removal efficiency of dyes can be found [18,19]. Therefore kapok fiber has to be treated to change to be hydrophilic before it is used to remove dyes from aqueous solution. Then the removal of lignin from kapok fiber may be favorable for the hydrophilic property [20] and ionic dye removal. It was reported that the treatment method with sodium chlorite ($NaClO_2$) under acidic condition was successfully employed by several groups to remove lignin from natural materials [20,21] and thus the method was used to treat kapok fiber in this study.

Response surface methodology (RSM), involving statistical design of experiments based on the multivariate non-linear model in which all factors are varied over a set of experimental runs, is a combination of mathematical and statistical techniques useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of some affecting factors even in the presence of complex interactions [22,23]. In this case, RSM makes treatment process modeling simple and efficient in the light of time and resource utilization. RSM has been widely used for optimization of the process variables of adsorption [24,25]. Nevertheless, in these publications, the optimization process is generally conducted to investigate the effects of several process parameters such as initial pH, initial concentration, temperature and adsorbent dose on the adsorption. To the best of our knowledge, little information about applying RSM to optimize the process parameters for obtaining an adsorbent with desired properties was reported.

In this study, RSM combined with Box–Behnken design was used to optimize the treatment process of kapok fiber by $NaClO_2$ rather than adsorption parameters and thus appropriate treatment conditions with maximum adsorption capacity for an adsorbate were obtained. Methylene blue (MB), as a representative of cationic dyes, is usually used in textile dyeing as its high affinity for solid surface and thus was employed as the model to test the adsorption behaviors of treated kapok fiber in the present study. By the use of three-level three-factorial Box–Behnken design and a full range of RSM, the following parameters were optimized: $NaClO_2$ content, HAc content, and reaction temperature. A second-order polynomial regression model was used to generate three-dimensional response surfaces of the adsorption capacity for MB. The regression model would provide a good explanation of the relationship between the independent variables and the response. Furthermore, the adsorption kinetics and effect of pH of MB solution on adsorption were investigated and adsorption mechanism was also proposed. The reusability of treated kapok fiber for MB removal was examined.

## 2. Experimental

### 2.1. Materials

Sodium chlorite was bought from Beijing Warwick Chemical Co. Ltd. (Beijing). Kapok fiber was provided by Shanghai Panda Industry Co. Ltd. (Shanghai). Methylene blue (MB, indicator grade) was provided by Alfa Aesar A Johnson Matthey Company and used as received.

### 2.2. Preparation of treated kapok fiber by $NaClO_2$

According to the matrix designed by Box–Behnken experimental design, an appropriate amount of $NaClO_2$ was dissolved in 100 mL of distilled water in a three-neck flask, while a required amount of HAc was added and stirred. Afterwards, 1.50 g of kapok fiber was added and stirred for 60 min at 700 rpm with designed reaction temperature. The treated kapok fiber was washed with distilled water until the filtrate reached pH 6–7, then dried at 70 °C to a constant weight, screened through a 20-mesh sieve and put in a desiccator for further use. The product was whiter than the pristine kapok fiber due to the bleaching property of $NaClO_2$.

**Table 1**
Independence factors and corresponding levels used for optimization.

| Variables | Real values of coded levels | | |
|---|---|---|---|
| | −1 | 0 | +1 |
| $NaClO_2$ content, $x_1$ (g) | 0.3 | 0.75 | 1.2 |
| HAc content, $x_2$ (mL) | 0.1 | 1.0 | 1.9 |
| Reaction temperature, $x_3$ (°C) | 60 | 75 | 90 |

### 2.3. Experimental design

The three-level, three-factorial Box–Behnken experimental design with categoric factor of 0 was employed to optimize the treatment process based on the adsorption capacity of the treated kapok fiber for MB (response). The design was composed of three levels (low, medium and high, being coded as −1, 0 and +1) and a total of 17 runs were carried out in duplicate to optimize the level of chosen variables, such as $NaClO_2$ content, HAc content and reaction temperature. For the purpose of statistical computations, the three independent variables were denoted as $x_1$, $x_2$, and $x_3$, respectively. According to the preliminary experiments, the range and levels used in the experiments are selected and listed in Table 1.

The experimental design matrix by the Box–Behnken design is tabulated in Table 2 and corresponding experiments were performed. The results were analyzed by applying the coefficient of determination ($R^2$), response plots and analysis of variance (ANOVA). For RSM, the most commonly used second-order polynomial equation developed to fit the experimental data and determine the relevant model terms can be written as:

$$Y_{\text{predicted}} = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

where $Y_{\text{predicted}}$ represents the predicted response, i.e. the adsorption capacity for MB by the treated kapok fiber (mg/g), $\beta_0$, the constant coefficient, $\beta_i$, the $i$th linear coefficient of the input factor $x_i$, $\beta_{ii}$, the $i$th quadratic coefficient of the input factors $x_i$, $\beta_{ij}$, the different interaction coefficients between input factors $x_i$ and $x_j$ ($i = 1$–$3$, $j = 1$–$3$ and $i \neq j$), and $\varepsilon$, the error of the model [26]. The equation expresses the relationship between the predicted response and independent variables in coded values according to Tables 1 and 2.

### 2.4. Adsorption experiments

Firstly, in a 100 mL conical flask, 0.050 g adsorbent was suspended in 25 mL of distilled water for 30 min with continuous shaking to make the adsorbent fully wet. And then, for each run, 25 mL of MB solution of 300 mg/L with natural pH was placed in the flask with a stopper and then agitated on a thermostatic shaker (THZ-98A) for 360 min at a constant speed of 120 rpm at 30 °C and corresponding adsorption capacity can be obtained. According to statistical analysis, the optimum conditions for the treated kapok fiber were obtained and corresponding treated kapok fiber was used to evaluate the effects of contact time, pH on adsorption and the reusability of the adsorbent. For kinetics studies, the two concentrations, 0 and 0.5 mmol/L, were applied for sodium dodecyl sulfate (SDS) in MB solution, and the treated kapok fiber was withdrawn from the flasks at predetermined time intervals until 360 min. For the test of effect of pH on adsorption, the pH of the MB solution was adjusted by the addition of a small amount of 0.1 mol/L

**Table 2**
Box–Behnken design matrix and corresponding experimental and predicted responses.

| Runs | $NaClO_2$ content (g) | HAc content (mL) | Reaction temperature (°C) | $Y_{experimental}$ (mg/g) | $Y_{predicted}$ (mg/g) |
|---|---|---|---|---|---|
| 1 | 0.3 | 1.9 | 75 | 88.89 | 88.56 |
| 2 | 0.75 | 1 | 75 | 97.57 | 97.57 |
| 3 | 0.3 | 1 | 90 | 96.45 | 96.79 |
| 4 | 0.75 | 1 | 75 | 97.57 | 97.57 |
| 5 | 1.2 | 0.1 | 75 | 91.18 | 91.51 |
| 6 | 1.2 | 1.9 | 75 | 94.92 | 94.28 |
| 7 | 0.75 | 1.9 | 90 | 103.83 | 103.82 |
| 8 | 0.3 | 1 | 60 | 84.76 | 84.11 |
| 9 | 0.3 | 0.1 | 75 | 84.15 | 84.79 |
| 10 | 0.75 | 1 | 75 | 97.57 | 97.57 |
| 11 | 0.75 | 1.9 | 60 | 85.91 | 86.90 |
| 12 | 0.75 | 1 | 75 | 97.57 | 97.57 |
| 13 | 0.75 | 0.1 | 90 | 97.56 | 96.57 |
| 14 | 1.2 | 1 | 60 | 90.42 | 90.08 |
| 15 | 0.75 | 0.1 | 60 | 87.61 | 87.62 |
| 16 | 1.2 | 1 | 90 | 102.61 | 103.26 |
| 17 | 0.75 | 1 | 75 | 97.57 | 97.57 |

of hydrochloric acid or sodium hydroxide solution. The MB solution with pH in the range of 2.0–10.0 with a 2.0 increment was stirred for 360 min. The residual MB concentration was analyzed with a Specord 200UV/vis spectrophotometer at the wavelength of 670 nm at which the maximum absorbency occurred. The adsorption capacity of the treated kapok fiber ($q_t$, mg/g) at any time $t$ was determined based on the following equation:

$$q_t = (C_0 - C_t)\frac{V}{W} \quad (2)$$

where $C_0$ and $C_t$ (mg/L) are the initial and final concentration of MB solution, respectively, $V$ (L), the volume of MB solution used and $W$ (g), the weight of the adsorbent used in the present study.

### 2.5. Desorption and regeneration studies

Desorption of MB loaded on the treated kapok fiber was conducted using 0.1 mol/L of hydrochloric acid as the desorbing agent. A fixed amount (50 mg) of the adsorbent was contacted with 50 mL diluted hydrochloric acid solution. The flask was placed in a thermostatic shaker for 120 min at 120 rpm. At the end of the experiment, the supernatant was collected to measure the desorbed amount for MB and the adsorbent was washed with distilled water for several times. And then, the recovered adsorbent was used in the subsequent five-cycle adsorption–desorption experiments.

### 2.6. Bioabsorbent characterization

The determination of the point of zero charge ($pH_z$) was carried out to investigate the surface charge of treated kapok fiber by the method depicted elsewhere [27,28]. For the determination of $pH_z$, 0.1 mol/L of potassium chloride was prepared and the pH was adjusted between 2.0 and 12.0 using diluted hydrochloric acid or sodium hydroxide solution. Then, 50 mL of 0.1 mol/L of potassium chloride solution was placed in a 100 mL conical flask and 0.05 g of treated kapok fiber was added to each solution. These flasks were kept for 24 h and the final pH values of the solutions were measured. Graph was plotted between final pH and initial pH. FTIR spectra of the samples were recorded on a Nicolet NEXUS FTIR spectrometer using potassium bromide pellets. The surface morphologies were determined using a JSM-5600LV SEM instrument (JEOL) with gold film. The specific surface area (SA) and pore size (PZ) of the samples were analyzed using an Accelerated Surface Area and Porosimetry System (Micromeritics, ASAP 202, Atlanta, USA) with $N_2$ as an adsorbate at 77 K.

## 3. Results and discussion

### 3.1. FTIR spectra analysis

FTIR spectra are commonly used to identify the groups involved in the reaction process and thus the FTIR spectra of pristine and treated kapok fiber are investigated and shown in Fig. 1. It was reported that under acidic condition, the $NaClO_2$ would produce chlorine dioxide, which rendered the oxidation of lignin [21]. The broad band at about 3397 $cm^{-1}$ ascribed to the stretching vibration of —OH in cellulose, became broader after treatment, which may be due to part of hydrogen bonds and lignin was broken, thus leading to increase in the amorphous part in cellulose and release of more hydroxyl groups. The band at 1643 $cm^{-1}$ may correspond to bending vibration of the water molecules and it had almost no change after treatment. The absorption bands at 1592, 1504 and 1463 $cm^{-1}$, were corresponding to stretching vibration of C—C in different substituted aromatic rings in lignin, and almost disappeared. The absorption band at 831 $cm^{-1}$, ascribed to the wagging vibration of C—H in 1,4-disubstituted aromatic ring in lignin, almost disappeared after treatment. All the information indicated that lignin in the kapok fiber was broken by the treatment. Furthermore, it can be also validated by the fact that the treated kapok fiber exhibited good hydrophilic property and it was fully wet after stirred with distilled water for 30 min. However, the pristine kapok fiber was always floated on the distilled water although it was stirred for 48 h.

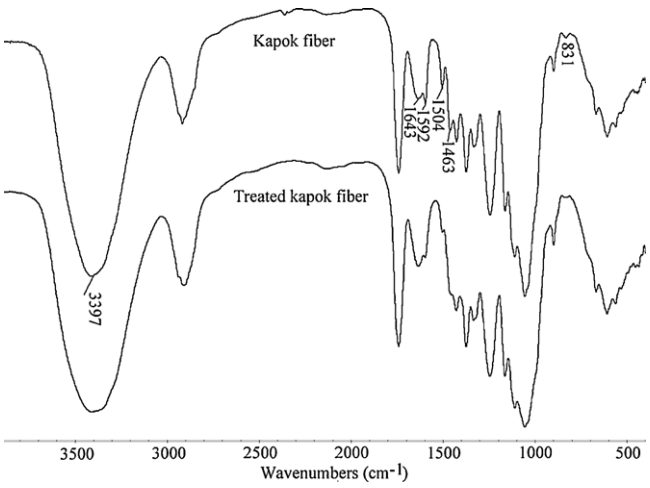


**Fig. 1.** FTIR spectra of kapok fiber before and after treatment with $NaClO_2$.

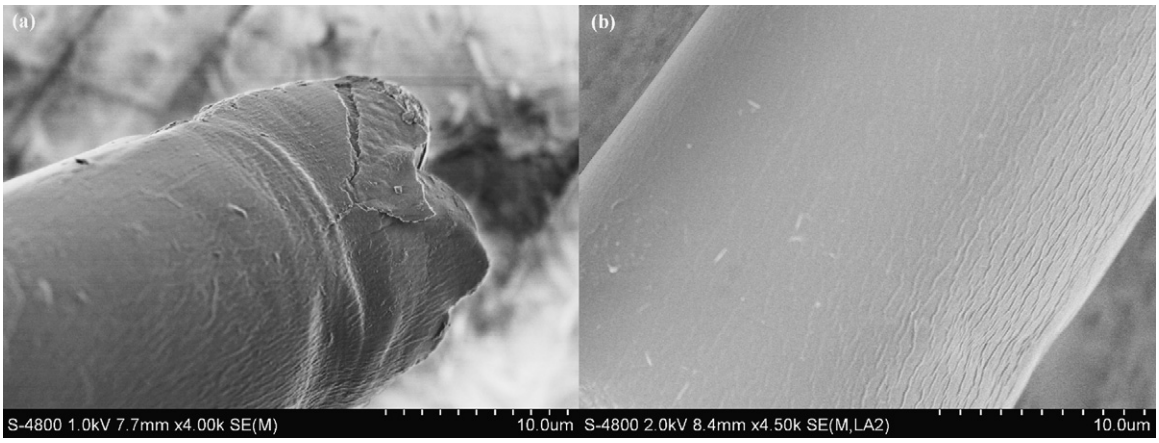


**Fig. 2.** SEM micrographs of pristine (a) and treated kapok fiber by $NaClO_2$ (b).

### 3.2. SEM analysis

To study the surface morphology, SEM micrographs of pristine and treated kapok fiber are shown in Fig. 2. The tube shape of pristine kapok fiber can be observed in Fig. 2(a). Furthermore, it was retained by the treatment with $NaClO_2$, as can be seen in Fig. 2(b), indicating the treatment would not damage the tube structure and surface fiber of kapok fiber. The result was similar to that reported before [20].

### 3.3. Statistical analysis

The adsorption experiments are conducted according to the design matrix and corresponding results are listed in Table 2. The quadratic equation for predicting the optimum point was obtained according to the Box–Behnken design and input variables, and then the empirical relationship between the response and the independent variables in the coded units was presented on the basis of the experimental results as follows:

$$Y_{\text{predicted}} = 97.57 + 3.11x_1 + 1.63x_2 + 6.47x_3 - 0.25x_1x_2 + 0.12x_1x_3 + 1.99x_2x_3 - 3.98x_1^2 - 3.81x_2^2 - 0.034x_3^2 \quad (3)$$

The results of the analysis of variance (ANOVA) for the quadratic equation are tabulated in Table 3. The ANOVA indicates the equation and actual relationship between the response and significant variables represented by the equation are accurate. The significance of the coefficient term is determined by the values of $F$ and $p$, and the larger the value of $F$ and the smaller the value of $p$, the more significant is [29,30]. The p is lower than 0.05, suggesting the model is considered to be statistically significant [31]. For the treated kapok fiber-MB system, the ANOVA results indicated the $F$-value for the model was 111.21, suggesting that only a 0.01% chance of a "Model $F$-value" so large could occur due to noise and the most of the variation in the response could be explained by the regression equation and that the model was significant. In addition, the probability $p < 0.0001$ also validated the model was significant. In the present investigation, $x_1$, $x_3$, $x_1^2$ and $x_2^2$ were highly significant parameters, while $x_2$ and $x_2x_3$ were significant factors. The other model terms, whose values of $p$ were higher than 0.1000 in Table 3, were not significant. Based on the analysis of Eq. (3) depicted that the variables $x_1$, $x_2$ and $x_3$ exhibited a positive relationship in the MB removal by the treated kapok fiber [32]. On checking the $R^2$ values, the "Predicted $R^2$" of 0.8889 was in reasonable agreement with the "Adjusted $R^2$" of 0.9841. "Adequacy Precision" measures the signal to noise ratio. It is reported that a ratio greater than 4 is desirable. The ratio of 33.61 suggested an adequate signal [33]. As analyzed above, this model can be used to navigate the design space.

The data were analyzed to examine the correlation between the experimental ($Y_{\text{experimental}}$) and predicted responses, as given in Fig. 3. As can be seen that the data points were well distributed close to a straight line ($R^2 = 0.9926$), which suggested an excellent relationship between the experimental and predicted values of the response, and the underlying assumptions of the above analysis were appropriate. The results also indicated that the selected quadratic model was adequate in assuming the response variables for the experimental data.

### 3.4. Three-dimensional response surface plot

Adsorption capacity for MB as the response, the three-dimensional response surface plots are shown in Fig. 4. It was obvious that adsorption capacity for MB was sensitive to $NaClO_2$ content, HAc content and reaction temperature, which was consistent with those analyzed about Table 3.

Fig. 4(a) depicted the three-dimensional response surface relationship between $NaClO_2$ content and HAc content on the MB removal by the treated kapok fiber at a constant reaction temperature of 75 °C. The MB removal increased from 84.15 to 90.05 mg/g and then decreased to 88.89 mg/g at $NaClO_2$ content of 0.3 g when HAc content increased from 0.1 to 1.9 mL. The adsorption capacity

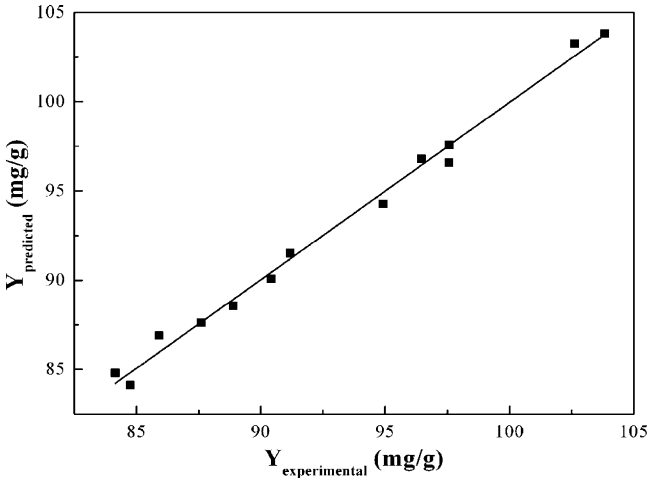


**Fig. 3.** Plot of the experimental and predicted responses.

**Table 3**
ANOVA for response surface quadratic model for MB removal by the treated kapok fiber.

| Source | Sum of squares | df | Mean square | *F* value | *p*-ValueProb > *F* | |
|---|---|---|---|---|---|---|
| Model | 585.27 | 9 | 65.03 | 111.21 | <0.0001 | Significant |
| $x_1$-$NaClO_2$ content | 77.38 | 1 | 77.38 | 132.33 | <0.0001 | Significant |
| $x_2$-HAc content | 21.29 | 1 | 21.29 | 36.41 | 0.0005 | Significant |
| $x_3$-temperature | 334.76 | 1 | 334.76 | 572.48 | <0.0001 | Significant |
| $x_1x$ | 0.25 | 1 | 0.25 | 0.43 | 0.5341 | |
| $x_1x$ | 0.06 | 1 | 0.06 | 0.11 | 0.7533 | |
| $x_2x$ | 15.88 | 1 | 15.88 | 27.16 | 0.0012 | Significant |
| $x_1^2$ | 66.57 | 1 | 66.57 | 113.85 | <0.0001 | Significant |
| $x_2^2$ | 61.08 | 1 | 61.08 | 104.46 | <0.0001 | Significant |
| $x_3^2$ | 0.0048 | 1 | 0.0048 | 0.0082 | 0.9304 | |
| Residual | 4.0932 | 7 | 0.5847 | | | |
| Lack of fit | 4.0932 | 3 | 1.3644 | | | |
| Pure error | 0 | 4 | 0 | | | |
| Cor total | 589.3657 | 16 | | | | |

for MB increased from 84.15 to 91.18 mg/g at HAc content of 0.1 mL as $NaClO_2$ content increased from 0.3 to 1.2 g. The effect of reaction temperature-HAc content was such that, the MB removal decreased from 97.56 to 87.61 mg/g at HAc content of 0.1 mL as reaction temperature decreased from 90 to 60 °C (Fig. 4(b) at a constant $NaClO_2$ content of 0.75 g), indicating high reaction temperature was favorable for the enhancement in the adsorption capacity of the treated kapok fiber. The effects of reaction temperature and $NaClO_2$ content (Fig. 4(c) at a constant HAc content of 1.0 mL) are same to that in Fig. 4(a) and (b). The information indicated that appropriate $NaClO_2$ content, HAc content and reaction temperature would render treated kapok fiber with higher adsorption capacity for MB and optimum conditions for treated kapok fiber could be obtain.

From the regression Eq. (3) and Fig. 4, the optimum treatment conditions for $NaClO_2$ content, HAc content, reaction temperature were obtained as below: $NaClO_2$ of 0.93 g, HAc of 1.42 mL and reaction temperature of 90 °C, under which the treated kapok fiber was expected to have maximum adsorption capacity for MB (105.48 mg/g). And the actual adsorption capacity of treated kapok fiber prepared under the optimum conditions for MB was determined to be 110.13 mg/g, very close to the predicted value. The treated kapok fiber prepared under optimum conditions was used further to test its adsorption properties for MB in detail.

### 3.5. Adsorption kinetics

Adsorption kinetic study is very important characteristic in water treatment as it depicts the adsorbate uptake rate, which in turn controls the residence time of adsorbate uptake at the solid–solution interface. In addition, surfactants, especially anionic surfactants, are commonly used in various industrial branches, mainly in the dyes manufacturing and textile finishing and they were commonly present in real wastewaters. Effects of contact time and SDS on adsorption are investigated, as shown in Fig. 5. The adsorption process was quite rapid and reached equilibrium in 60 min (Fig. 5) in the absence of SDS, meaning a fast adsorption process. However, the adsorption process was a little slow and reached equilibrium in 240 min in the presence of SDS. When the treated kapok fiber immerged in distilled water, the water molecules would penetrate quickly into the fiber, and the concentration gradient of MB was formed as the addition of MB solution. After $NaClO_2$ treatment, the surface of kapok fiber had changed from hydrophobic to hydrophilic, as a result of the cleavage of part of the phenolic compounds and the removal of waxy cutin [20]. In addition, the interaction of celluloses was broken, and thus many activated points were available for MB, leading to high adsorption efficiency, compared to pristine kapok fiber with almost no adsorption efficiency due to its hydrophobic property. Furthermore, according to the Brunauer–Emmett–Teller (BET) analysis, the values in SA of pristine and treated kapok fiber were 7.19 and 4.90 $m^2$/g, respectively. The values in PZ of pristine and treated kapok fiber were 4.39 and 5.37 nm, respectively. The results validated that the interaction of cellulose was broken, thus leading to higher PZ value, lower SA value and higher removal efficiency for MB after treatment. In the presence of SDS, owing to the interaction between the treated kapok fiber and SDS, the adsorption sites in the inner of the adsorbent was more difficult to be contacted with MB, thus leading to a lower adsorption rate and more time to reach adsorption equilibrium. However, the adsorption capacity was higher in the presence of SDS than that without SDS. This may be ascribed to that SDS can be relatively strongly bound with some kinds of nonpolar sorbents, leading to increase in the negative sites and thus leading to high removal efficiency [34]. The result was similar to that reported before [35].

Adsorption kinetic data were analyzed using pseudo-first-order and pseudo-second-order kinetic equations, which were given as [36,37]:

$$\ln(q_{1e} - q_t) = \ln\ q_{1e} - k_1 t \tag{4}$$

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

where $q_{1e}$ or $q_{2e}$ represents the adsorption capacity of the treated kapok fiber at equilibrium (mg/g), $k_1$ ($min^{-1}$) and $k_2$ (g/(mg min)), the rate constants of pseudo-first-order and pseudo-second-order kinetics equations, respectively.

For pseudo-second-order kinetics, the initial adsorption rate $h$, (mg/(g min)) can be calculated according to the following equation [38]:

$$h = k_2 {q_{2e}}^2 \tag{6}$$

The initial adsorption rate is commonly used as a measure of the adsorption rate.

The corresponding parameters calculated and experimental adsorption capacities are obtained and tabulated in Table 4. It can be seen that the correlation coefficients from pseudo-second-order kinetics were higher than those from pseudo-first-order kinetics and the experimental adsorption capacities ($q_{exp}$) were close to theoretical adsorption capacities calculated from pseudo-second-order kinetic equation, indicating pseudo-second-order kinetics could reasonably describe the adsorption process. The values of $k_2$ and $h$ of the adsorption system in the absence of SDS were higher than those in the presence of SDS, validating the slower adsorption process of the latter system.

In addition, the experimental capacities for MB onto various absorbents according to kinetic studies were studied, as shown in Table 5. It can be seen that the treated kapok fiber showed higher adsorption capacity for MB than other adsorbents tabulated in the

**Table 4**
Kinetic parameters and experimental adsorption capacities for MB onto the treated kapok fiber.

| SDS (mmol/L) | $q_{exp}$ (mg/g) | Pseudo-first-order model | | | Pseudo-second-order model | | | |
|---|---|---|---|---|---|---|---|---|
| | | $q_{1e}$ (mg/g) | $k_1 \times 10^2$ ($min^{-1}$) | $R^2$ | $q_{2e}$ (mg/g) | $k_2 \times 10^3$ (g/(mg min)) | $h$ (mg/(g min)) | $R^2$ |
| 0 | 110.13 | 37.00 | 1.53 | 0.7745 | 110.13 | 3.44 | 41.72 | 0.9998 |
| 0.5 | 139.88 | 72.70 | 1.22 | 0.9336 | 139.28 | 1.12 | 21.67 | 0.9963 |

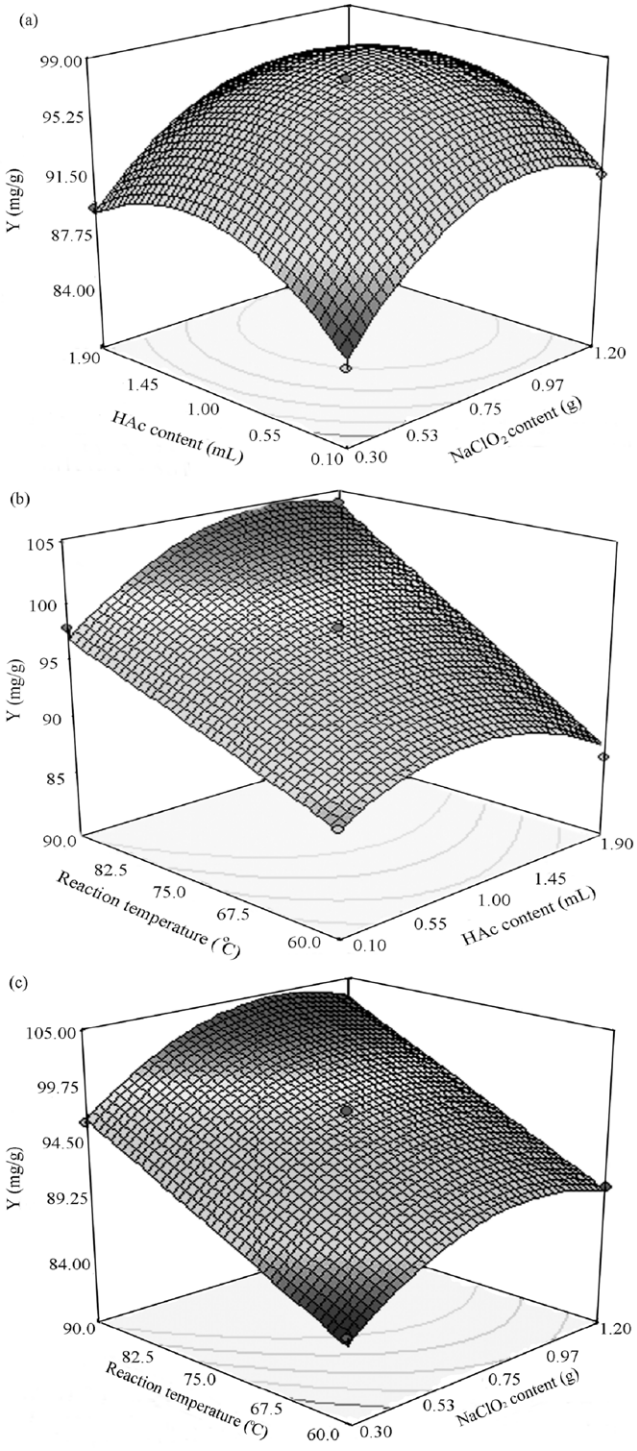


**Fig. 4.** Response surface plots of adsorption capacity versus the effect of variables of (a) $x_1x_2$, (b) $x_2x_3$, (c) $x_1x_3$.

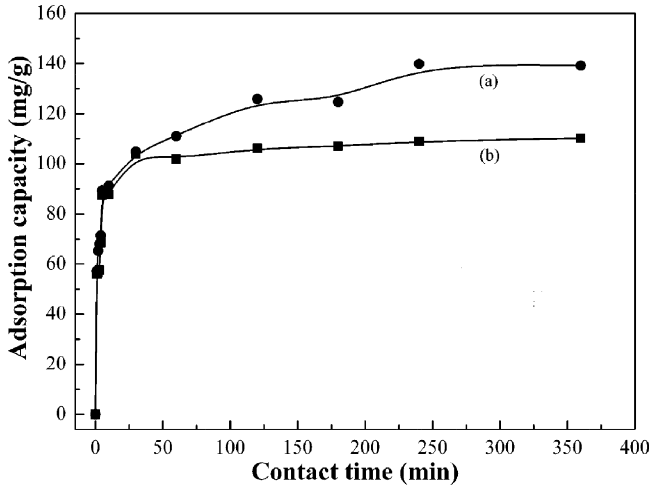


**Fig. 5.** The plot of adsorption capacity for MB versus contact time in the presence of SDS (a) and absence of SDS (b).

table, indicating it exhibited great potential as an adsorbent for MB removal.

### 3.6. Effect of pH on adsorption

In general, pH is one of the most significant parameters influencing the adsorption process. To evaluate the effect of pH on MB uptake, experiments were conducted using various pH levels in the range of 2.0–10.0, as depicted in Fig. 6(a). It was clear that the adsorption capacity remarkably increased as increasing pH value until pH = 6.0 and then gradually increased. The phenomenon can be explained by the $pH_z$ of the treated kapok fiber. Graph was plotted between final pH and initial pH, as shown in Fig. 6(b). The point of intersection of the curve of final pH versus initial pH was recorded as $pH_z$ of the treated kapok fiber. Thus, the $pH_z$ of the treated kapok fiber was found to be 5.8, and therefore at pH values greater than $pH_z$, the removal efficiency must be higher, as validated by Fig. 6(a). It may be due to that as pH of MB solution increased from 6.0 to 10.0, the deprotonation of hydroxyl groups on the surface of the treated kapok fiber increased, thus leading to increase in electrostatic attraction and higher adsorption capacity for MB, which was consistent with the report before [15].

**Table 5**
The experimental capacities for MB onto various absorbents according to kinetic study.

| Samples | Adsorption capacity (mg/g) | Reference |
|---|---|---|
| Sepiolite | 67.30 | [6] |
| Banana peel | <12 | [7] |
| Orange peel | <7 | [7] |
| Pistachio hull waste | 66.5 | [8] |
| Giant duckweed | 57.03 | [39] |
| Treated kapok fiber | 110.13 | This work |

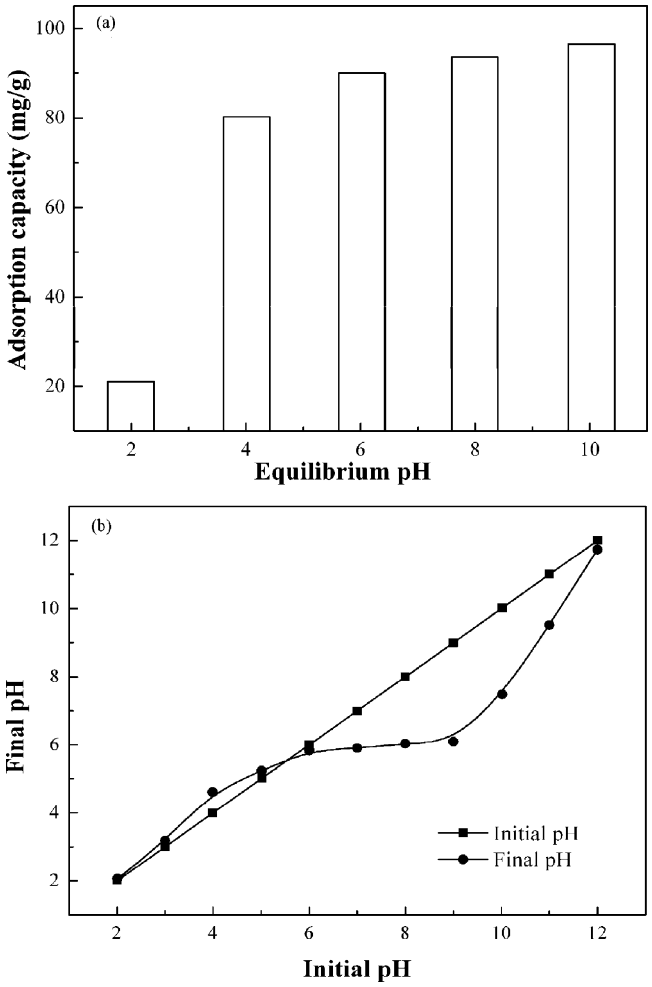


**Fig. 6.** Effect of pH on adsorption (a) and initial pH versus final pH for determination of $pH_z$ of the treated kapok fiber (b).

### 3.7. Adsorption mechanism

Shifts or changes of FTIR peaks suggest interaction of the solute with functional groups on the surface of the adsorbent. The FTIR spectra of treated kapok fiber before and after adsorption and MB are shown in Fig. 7. The band at 1602 $cm^{-1}$, ascribed to

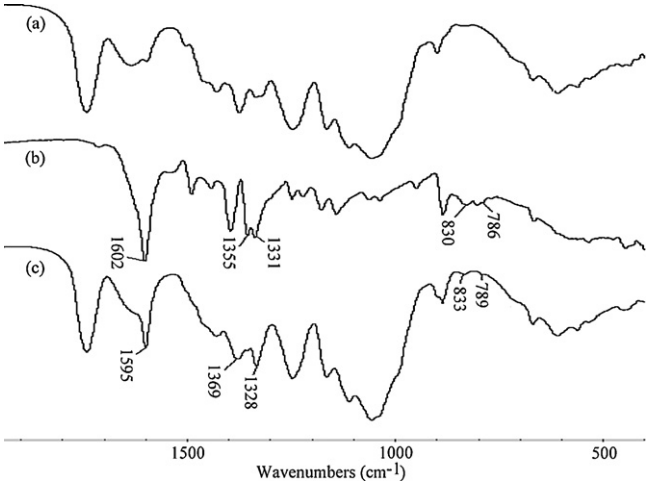


**Fig. 7.** FTIR spectra of treated kapok fiber (a), MB (b) and MB loaded treated kapok fiber (c).

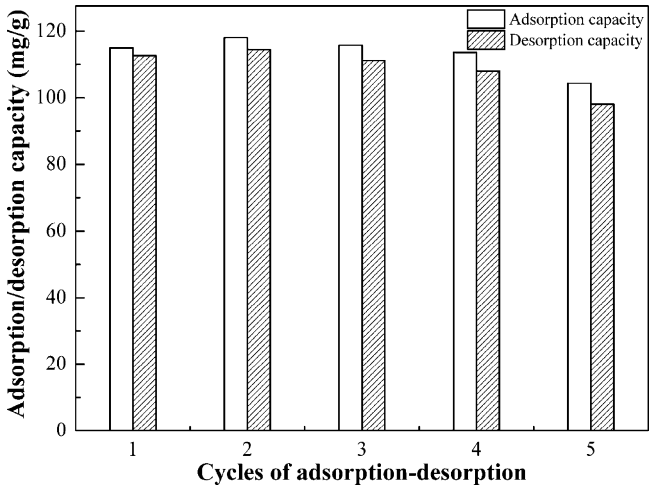


**Fig. 8.** Reusability of the treated kapok fiber.

stretching vibration of C—C in aromatic ring (Fig. 7(b)), appeared and shifted to low wavenumber in the spectra of treated kapok fiber after adsorption. The absorption bands at 1355 and 1331 $cm^{-1}$ were corresponding to the stretching vibration of C—N in MB, the first of which shifted after being adsorbed. New bands (830 and 786 $cm^{-1}$), were ascribed to wagging vibration of C—H in aromatic ring of MB and appeared in the spectra of treated kapok fiber after adsorption. The information indicated that the formation of hydrogen bond between surface of the treated kapok fiber and nitrogen, sulfur and aromatic ring of MB molecules and electrostatic attraction dominated the adsorption process.

### 3.8. Desorption and reusability

An excellent adsorbent must exhibit reusability except high adsorption capacity and rapid adsorption rate from view of practical application. It was found that MB onto the treated kapok fiber could be well desorbed by 0.1 mol/L hydrochloric acid solution according to preliminary experiments. As the spent adsorbent was recovered, the reusability was examined and corresponding results are shown in Fig. 8. It can be seen that after five adsorption–desorption cycles, no significant loss in the adsorption capacity was observed and the adsorption capacity of the fifth cycle only reduced by 9.29% compared to that of the first cycle. Furthermore, it can be seen that the desorption capacities were very high with desorption efficiency of more than 90%. The results indicated that the treated kapok fiber was effective and efficient adsorbent for MB removal.

## 4. Conclusions

RSM was employed to optimize the treatment parameters to obtain hydrophilic kapok fiber with good adsorption properties for MB. The optimum treatment conditions of $NaClO_2$ of 0.93 g, HAc of 1.42 mL and reaction temperature of 90 °C were obtained through the statistical analysis. The three parameters were significant factors affecting the adsorption capacity for MB. The adsorption kinetics suggested that the adsorption process was fast and reached equilibrium in 60 min. The treated kapok fiber was found to be pH dependent. Through the FTIR analysis, formation of hydrogen bonds and electrostatic attraction dominated the adsorption process. The MB loaded treated kapok fiber could be effectively desorbed by diluted hydrochloric acid solution and the recovered adsorbent exhibited excellent reusability. All the information indicated that

the treated kapok fiber exhibited potential applications in the fields of wastewater treatment for the removal of cationic dyes.

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