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Adsorption of crystal violet onto amino silica: optimization, equilibrium, and kinetic studies

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ABSTRACT

Adsorption of crystal violet (CV) onto amino silica (AS) was investigated as a function of parameters including aqueous pH, temperature, AS dose, contact time, agitation speed, and initial CV concentration. And the optimum conditions obtained from response surface methodology (RSM) were temperature 33℃, AS dosage 0.35 g, contact time 64 min, and agitation speed 230 rpm. The adsorption equilibrium using Langmuir and Freundlich models indicated that the process followed Langmuir isotherm and the maximum adsorption capacity reached 40 mg g^{-1}. After both pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental data, pseudo-second-order model was found describing the adsorption process very well.

Keywords: Adsorption; Amino silica; Crystal violet; Response surface methodology

1. Introduction

As a triphenylmethane dye, soluble in water, stable, and resistant toward light and chemical bleaches [1], crystal violet (CV) is widely used in the industry of biological stain, dermatological agent, veterinary medicine, additive, intestinal parasites and fungus, and it is also used as a pH indicator in nonaqueous titration. However, as inhalation, ingestion and skin contact results in heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis *etc*., it is commonly considered as a hazardous material. Thus, the removal of CV from effluents is a noteworthy object for environmentalists.

Over years, many methods like oxidation, flota-tion, coagulation, photochemical destruction, and biodegradation have been broadly researched for the removal of dyes from effluents [2–7]. Unfortunately, with expensive cost and exhausting large amount of chemicals which could bring about new pollutions, methods above are always inapplicable to large-scale units. As adsorption have the potential of regeneration of adsorbent and recovery of adsorbate [8], it has been a well-known separation technique for dye and organic removal. Amino silica (AS), with high specific surface, nontoxicity, and active functional groups, has received great attention as adsorbent. Donia et al. [9] investigated its adsorption behavior vs. acid orange 10 and acid orange 12. Andrzejewska et al. [10] reported the removal of C.I. Reactive Blue 19 using precipitated syloid® 244 silica modified with APTS. Shahbazi et al. [11] synthesized a functional SBA-15 mesoporous silica with amine and used it as an adsorbent for the

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removal of metal ions from aqueous solution. Cestari et al. [12,13] studied the interactions of anionic dyes (Reactive Red RB, Reactive Blue RN, and Reactive Yellow GR) with silica 60 modified with APTS and made a quantitative multivariate analysis of equilibrium adsorption and adsorption Gibbs free energies. Our group [14] have successfully adsorbed Alizarin Red S onto nano-sized silica modified with APTS.

Optimization of sorption of CV by the classical method involves changing one independent variable while maintaining all others at a fixed level which is extremely time-consuming and experimental for a large number of variables. To overcome this difficulty, Central Composite Design and response surface methodology (RSM) can be employed to optimize the sorption of CV. The objective of the present study is to optimize sorption of CV in aqueous solution onto AS. For better understanding of different stages of sorption at varying temperature, AS dosage, contact time and agitation speed, RSM was used to optimize CV uptake. And the adsorption kinetics of CV by AS was investigated at a constant adsorbent dosage and constant solution pH.

2. Experimental

2.1. Chemicals and instruments

2.1.1. Chemicals

Analytical grade Crystal Violet (CV, $C_{25}H_{30}ClN_3 \cdot 9H_2O$) was supplied by Sinopharm Chemical Reagent Co., Ltd., was utilizing without further purification. The chemical structure of CV is shown as Fig. 1. And CV dye exists as cation in aqueous medium. The pH value of the resulting solution was adjusted by using $1\,mol\,L^{-1}$ HCl and $1\,mol\,L^{-1}$ NaOH solutions.

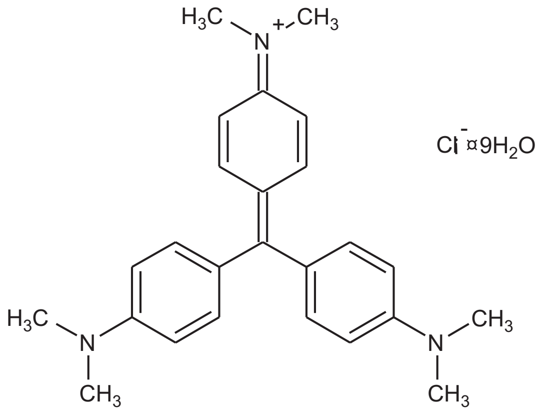

Fig. 1. Chemical structure of CV.

AS with particle size 20.6 nm, specific area $119.5\,m^2\,g^{-1}$ and amino content $1.35\,mmol\,g^{-1}$ was supplied by Henan Province Nanomaterial Engineering and Technology Research Center in China [14,15]. The structure of the AS is shown in Fig. 2.

All other reagents were analytical grade, and distilled water was applied throughout.

2.1.2. Instruments

A digital pH meter (HANNA Century Instruments Ltd., Italy) was used to measure the pH of the solution. The concentration of CV dye solution was determined using an ultraviolet–visible light (UV–vis) spectrophotometer (LabTech Ltd., Beijing, China) at a wave length of 581 nm. A mechanical stirrer (JJ-4A, Yingsheng Hengtai Technology Company Ltd., Beijing, China) was used to stir the solution. A centrifuge (Lab Centrifuge Company Ltd., Beijing, China) was used to separate AS particles from the dye samples collected from the solution.

2.2. Response surface methodology (RSM)

As a statistical experimental design for modeling and analyzing engineering problems by establishing continuous variable surface model, evaluating all possible factors and their interactions, then optimizing the operation conditions, RSM was employed to discuss the combined effects of temperature (X_1), adsorbent dosage (X_2), contact time (X_3), and agitation speed (X_4) on the removal of CV in this work. For statistical calculation, the code values of variables were presented according to Eq. (1).

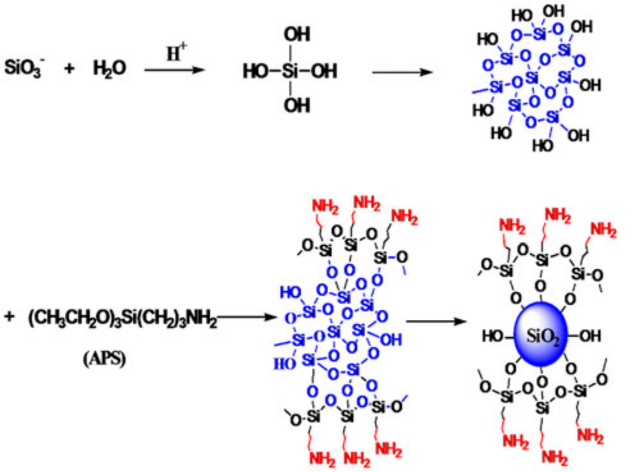

Fig. 2. The schematic illustration of formation mechanism of the AS.

Table 1
Levels of the dependent variables in coded and uncoded form

Variables	Code	Levels				
		−2	−1	0	1	2
Temperature (℃)	X_1	5	15	25	35	45
Adsorbent dosage (g/L)	X_2	10.0	16.7	23.3	30.0	36.7
Contact time (min)	X_3	20	40	60	80	100
Agitation speed (rpm)	X_4	50	100	150	200	250

$$x_i = \frac{X_i - X_0}{\Delta x} \tag{1}$$

where x_i is the independent variable coded value; X_i is the independent variable uncoded value; X_0 is the independent variable uncoded value at centre point; and Δx is the step change value. According to the single factor experiment, which carried out by our group [16], the range and levels of individual variables were given in Table 1.

The regression analysis for the four variables and response were evaluated by a second order polynomial Eq. (2).

$$Y_D = a_0 + \sum a_i X_i + \sum a_{ii} X_i^2 + \sum a_{ij} X_i X_j \tag{2}$$

where Y_D is the predicted response of percentage color removal by the model; a_0 is equation constant; and, a_i, a_{ii}, and a_{ij} are regression coefficients for the model. The experimental design is shown in Table 2 along with experimental data and predicted response.

2.3. Experimental procedure

A typical adsorption test was as follows. Certain amount of AS was added into 15 mL 200 mg L^{-1} CV working solution adjusted to desired pH by 20% HCl or 20% NaOH, then the mixture was agitated at a constant temperature water bath-vibrator (SHZ-B, Shanghai Yuejin Medical Instruments Factory) under the designed conditions of temperature, contact time, and agitation speed. The final mixture was centrifuged at 4,000 rpm for 30 min to disperse the AS particles. After that known volume supernatant solution was diluted with HAc-NaAc buffer solutions (pH = 4.47) and the residual CV was determined spectrophotometrically at 581 nm using a UV-2000 spectrometer (LabTech Ltd., Beijing, China). The percentage color removal of CV (Y,%) was calculated with Eq. (3).

$$Y(\%) = \frac{c_0 - c_e}{c_0} \times 100\% \tag{3}$$

The adsorption capacity of CV onto AS could be computed with Eq. (4).

$$q_e = \frac{(c_0 - c_e) \cdot V}{m} \tag{4}$$

where c_0 and c_e are the initial and residual concentrations of CV(mg L^{-1}), q_e is the adsorption capacity of CV on AS (mg g^{-1}); V is the volume of the CV working solution (L); and, m is the mass of AS (g).

3. Results and discussion

3.1. Analysis for response surface model

According to the experimental design (independent variables and their levels, in Table 1), 31 experiments (in Table 2) were performed to investigate the percentage color removal of CV by AS, and the experimental data were analyzed by MATLAB 7.0. Quadratic polynomial equation for the percentage color removal of CV was calculated to be Eq. (5) through multiple regression analysis.

$$\begin{aligned} Y_D = {} & 94.011 + 3.886X_1 + 1.842X_2 + 3.052X_3 \\ & + 3.063X_4 - 1.802X_1X_2 - 1.526X_1X_3 \\ & + 1.180X_1X_4 - 2.246X_2X_3 - 1.102X_2X_4 \\ & - 1.146X_3X_4 - 2.255X_1^2 - 0.773X_2^2 - 0.748X_3^2 \\ & - 3.079X_4^2 \end{aligned} \tag{5}$$

Analysis of variance (ANOVA) was used for estimating the quadratic regression model and results were given in Table 3. It can be seen that the model's F-statistical value was 7.36, indicating the importance of the model. Otherwise, P value is generally an important indicator of the significance of each interaction among the variables, and the smaller P value is, the more significant corresponding coefficient is. When P value is lower than 0.05, the model is statistically significant at 95% confidence level, which demonstrated that X_1, X_2, X_3, X_4, ${X_1}^2$, ${X_4}^2$, $X_2 \times X_3$ were significant model terms. Furthermore, the coeffi-

Table 2
Experimental design, experimental, and observed response values

Run no.	X_1	X_2	X_3	X_4	Percentage color removal (%)	
					Experimental	Response
1	0	0	0	0	94.04	94.01
2	0	0	2	0	92.37	97.12
3	0	0	−2	0	89.72	84.92
4	−1	−1	1	1	86.83	88.29
5	0	0	0	2	87.70	87.82
6	0	0	0	0	95.94	94.01
7	1	1	−1	1	94.77	96.09
8	−1	1	−1	1	83.99	86.51
9	1	−1	−1	1	94.54	93.72
10	−1	1	1	−1	87.97	89.61
11	0	0	0	0	93.43	94.01
12	−1	1	1	1	93.25	88.88
13	1	−1	1	−1	92.27	90.58
14	1	−1	−1	−1	77.15	80.74
15	1	1	1	−1	90.80	88.37
16	0	2	0	0	89.74	94.61
17	0	0	0	0	93.01	94.01
18	−1	−1	−1	−1	63.38	68.67
19	2	0	0	0	91.42	92.76
20	−1	1	−1	−1	85.93	82.66
21	1	−1	1	1	96.48	98.97
22	0	−2	0	0	92.15	87.24
23	0	0	0	0	92.50	94.01
24	−2	0	0	0	78.61	77.22
25	0	0	0	0	95.60	94.01
26	1	1	−1	−1	88.15	87.52
27	−1	−1	−1	1	75.28	76.93
28	0	0	0	−2	75.74	75.57
29	1	1	1	1	96.82	92.36
30	−1	−1	1	−1	86.71	84.61
31	0	0	0	0	93.56	94.01

cient of regression R^2 was calculated to be 0.8656, indicating a good fitness between the experimental data and the predicted values. The adjusted R^2 (Adj. R^2) was 0.7479, implying that 74.79% of variability in the response could be explained by the model. The results indicated the model was quite satisfactory.

On the basis of the model, three-dimensional response plots and contour plots were drawn and presented in Fig. 3. The mutual interactions among the variables could be gained from the shape of the corresponding contour plots. The elliptical shape of the curve indicated good interaction of the two variables and circular shape indicated no interaction between the variables [17]. It was observed that the mutual interactions between sorbent dosage and temperature, agitation speed and sorbent dosage, agitation speed and contact time were significant, while those between contact time and temperature, agitation speed and temperature, contact time and sorbent dosage were insignificant.

The sequential quadratic programming in MATLAB 7.0 was employed to solve the second-degree polynomial regression Eq. (5). The optimal values for the variables as predicted by MATLAB were found to be within the design region. This showed that the model correctly explains the influence of the chosen variables on the percentage color removal of CV. Combining the optimum values predicted by quadratic programming with actual conditions, the optimum values of test variables were selected as follows: temperature 33℃, adsorbent dosage 0.35 g, contact time 64 min, and agitation speed 230 rpm.

3.2. Effect of pH

pH was an important factor affecting the percentage color removal of CV. Therefore, a series of adsorption equilibrium experiments were conducted with CV solutions pH from 2.0 to 10.0 under the optimum conditions and the results were shown in Fig. 4. As seen, the percentage color removal increased with the increase in pH from 2.0 to 6.0 and then reached an approximately fixed value at the pH range of 6–10. In the present work, all experiments were carried out at pH 8.0.

3.3. Effect of initial dye concentration

Fig. 5 displayed the percentage color removal of CV at different initial concentrations within 50–800 $\mathrm{mg\,L^{-1}}$, accompanying with the corresponding adsorption capacity at equilibrium (q_e). As shown, the removal of CV suddenly increased to 98.9% as the initial CV concentration increased from 50 to 200 $\mathrm{mg\,L^{-1}}$ and then kept no significant change (around 99.3%) until the initial CV concentration increased to 800 $\mathrm{mg\,L^{-1}}$. Meanwhile, the q_e value increased with the increase in initial CV concentration linearly from 1.57 to 34.23 $\mathrm{mg\,g^{-1}}$. All results above indicated that the adsorption of CV increased with the increase in initial CV concentration. This might be attributed to that, a higher initial CV concentration could supply more CV molecules in aqueous solution, which could provide much stronger driving force to overcome mass transfer resistance on adsorbent surface; on the other hand, the increasing concentration of adsorbate

Table 3
Analysis of variance (ANOVA) for response surface quadratic model

Source	Sum of square	DF	Mean square	F	P
Model	1507.15	14	107.65	7.36	0.0001
X_1	362.39	1	362.39	24.77	0.0001
X_2	81.48	1	81.48	5.57	0.0313
X_3	223.50	1	223.50	15.28	0.0012
X_4	225.22	1	225.22	15.39	0.0012
X_1^2	100.87	1	100.87	6.90	0.0183
X_2^2	4.78	1	4.78	0.33	0.5754
X_3^2	5.10	1	5.10	0.35	0.5629
X_4^2	271.08	1	271.08	18.53	0.0005
$X_1 \times X_2$	51.98	1	51.98	3.55	0.0777
$X_1 \times X_3$	37.27	1	37.27	2.55	0.1300
$X_1 \times X_4$	22.28	1	22.28	1.52	0.2350
$X_2 \times X_3$	80.73	1	80.73	5.52	0.0320
$X_2 \times X_4$	19.45	1	19.45	1.33	0.2658
$X_3 \times X_4$	21.02	1	21.02	1.48	0.2481
Residuals	234.07	16	14.63		
Lack of fit	233.90				
Pure error	0.17				
Cor total	1741.22	30			

Note: Multiple R_2: 0.8656; Adjusted R_2: 0.7479; Standard deviation: 3.825.

in aqueous solution could enhance the interaction between adsorbent and adsorbate [14].

3.4. Adsorption isotherms

Langmuir and Freundlich, commonly known isotherm models, were employed to describe the adsorption equilibrium. The linearized Langmuir isotherm [18] could be represented as Eq. (6).

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m} \tag{6}$$

where q_m is the maximum adsorption capacity of the adsorbent ($\mathrm{mg\,g^{-1}}$); c_e is the equilibrium concentration of the adsorbate ($\mathrm{mg\,L^{-1}}$); and K_L is the Langmuir constant ($\mathrm{L{\cdot}mg^{-1}}$). The values of K_L and q_m could be calculated from the intercept and the slope by plotting c_e/q_e vs. c_e. The dimensionless separation factor R_L [19], which can be calculated as Eq. (7), can predict the affinity between the sorbent and adsorbent.

$$R_L = \frac{1}{1 + K_L c_0} \tag{7}$$

where c_0 is the initial concentration of the adsorbate ($\mathrm{mg\,L^{-1}}$).

The R_L classified as $R_L > 1$, $0 < R_L < 1$ and $R_L = 0$ suggests that adsotption is unfavorable, favorable and irreversible, respectively. The value of R_L for the present work was obtained as 0.3251, clearly indicating the favorability of the adsorption process [20].

The linearized Freundlich isotherm [21] is commonly given as Eq. (8).

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \tag{8}$$

where K_F is a Freundlich constant. The slope $1/n$, ranges in value from 0 to 1, is a measure of the adsorption intensity. Generally, the lower value of $1/n$ is, the more heterogeneous adsorption process is. The values of K_F and $1/n$ could be obtained by linearly fitting log q_e with log c_e. Table 4 listed the values of the parameters (q_m, K_L, K_F and n) of Langmuir and Freundlich models, as well as corresponding regression coefficient, R^2. It was obvious that R^2 in Langmuir model was 0.9772, evidently higher than that in Freundlich model, which was 0.8093. Therefore, it could be well considered that the Langmuir isotherm was more favorable to the adsorption process, indicating that the adsorption of CV onto AS was a monolayer molecular sorption process. Comparing the adsorption capacity exhibited in our work with those of adsorbents reported by other authors (Table 5) indi-

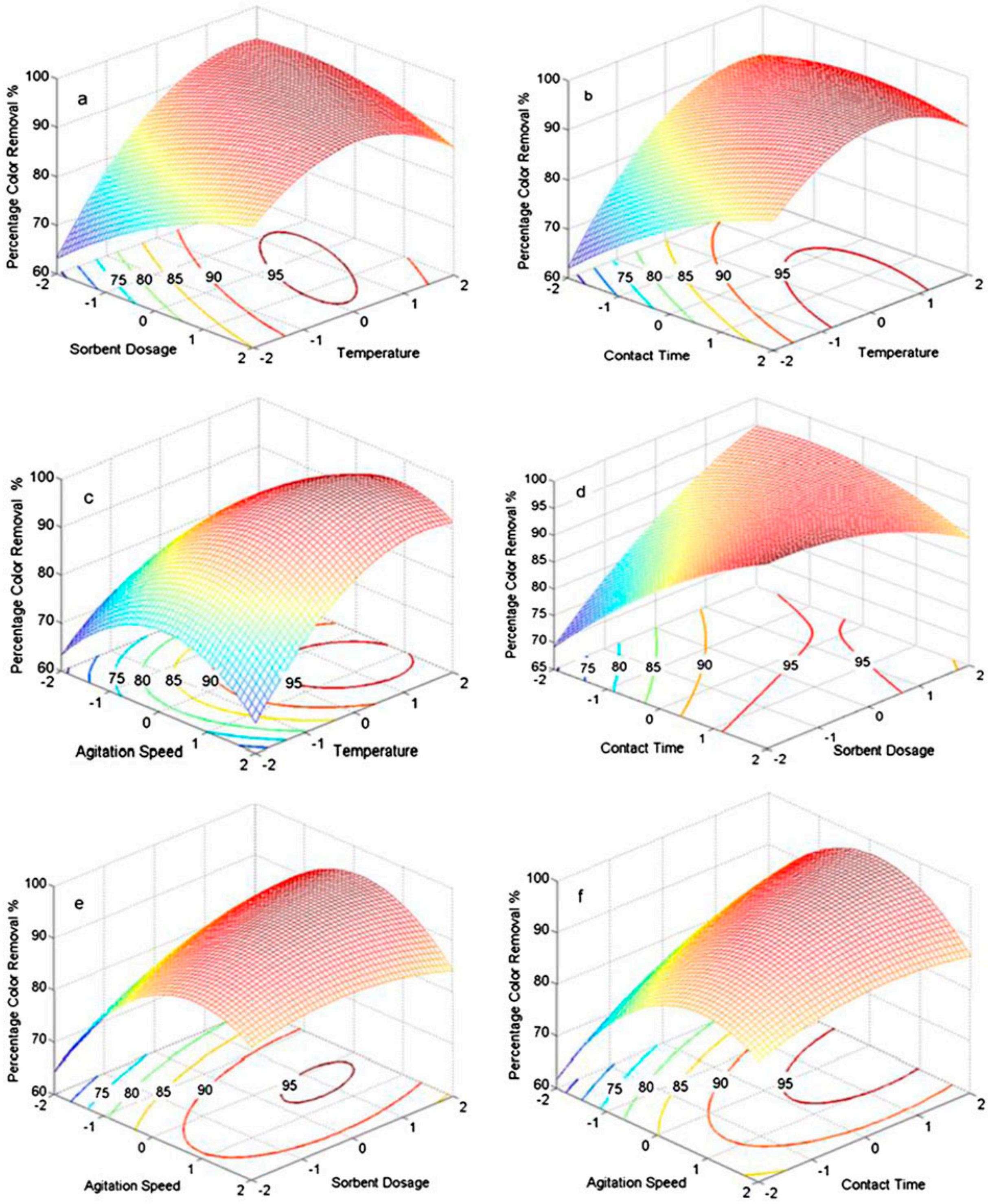

Fig. 3. Response surface plots of the combined effects of different variables on the percentage color removal of CV by AS. (a) temperature and sorbent dosage, (b) temperature and contact time, (c) temperature and agitation speed, (d) sorbent dosage and contact time, (e) sorbent dosage and agitation speed, and (f) contact time and agitation speed (pH 8.0 and initial dye concentration 200 mg/L).

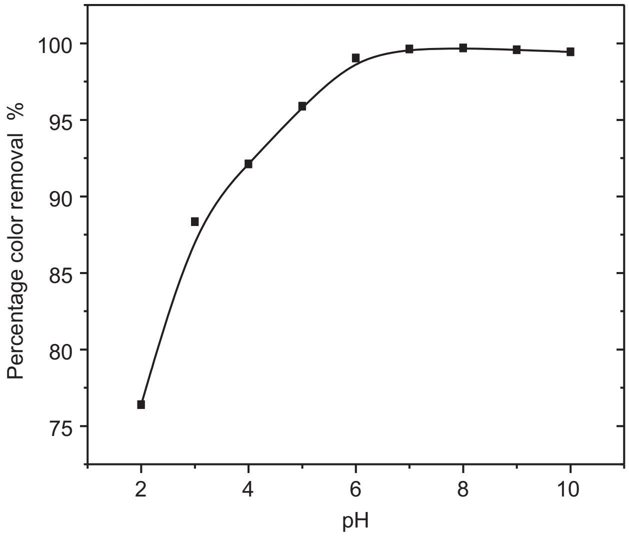

Fig. 4. Effect of pH on the percentage adsorption of CV. (Initial dye concentration 200 mg/L, sorbent dosage: 23.3 g/L, V: 15.0 mL, t: 64 min, temperature: 33 ℃).

cates that AS have good adsorption capacity on CV. And it is suitable to deal with high concentration wastewater of CV.

3.5. Adsorption kinetics

Pseudo-first-order and pseudo-second-order kinetics were both applied to estimate the order of the adsorption process. The pseudo-first-order kinetic equation [25] was represented as Eq. (9).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{9}$$

where k_1 is the pseudo first-order rate constant (min^{-1}); and, q_t is the amount of dye adsorbed at time t (mg g^{-1}).

The pseudo-second-order kinetic equation [26] was expressed as Eq. (10).

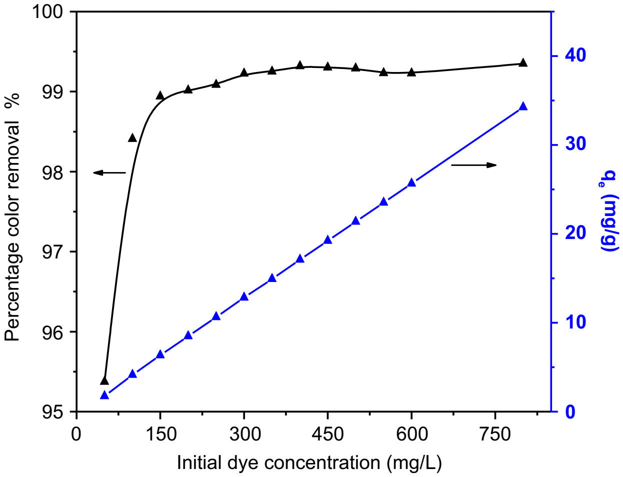

Fig. 5. Effect of initial dye concentration on adsorption of CV. (Initial pH: 8.0, sorbent dosage: 23.3 g/L, V: 15.0 mL, t: 64 min, temperature: 33 ℃).

Table 4
The isotherm parameters for dyes adsorption onto AS

	Langmuir				Freundlich		
	$q_{\max}$ (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	K_F (mg g^{-1})	n	R^2
CV	40.00	0.01038	0.3251	0.9772	3.3496	2.4450	0.8093

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

where k_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1}\,\text{min}^{-1}$).

The applicability of the two models above could be examined by comparing the regression coefficient (R^2) of the plots of $\log(q_e - q_t)$ against t (Fig. 6(a)) and t/q_t against t (Fig. 6(b)). As it was shown in Fig. 6, R^2 for pseudo-second-order model was 0.9998, while that of the pseudo-first-order model was 0.8488, which

Table 5
Comparison of adsorption capacities of various adsorbents for CV

Adsorbents	Adsorbent dose (g/L)	Modifier agent	CV concentration (mg/L)	Solution pH	T (℃)	q_m (mg/g)	Ref.
HTS	2.4	Hydrotalcite gel	30	–		11.2	[22]
Jute fiber carbon	1.0	–	40	10	30	27.99	[23]
Artocarpus heterophyllu	10.0	–	50	7.0	20	43.39	[24]
AS	23.3	3-Aminopropyltriethoxysilane	200	8.0	33	40.00	This work

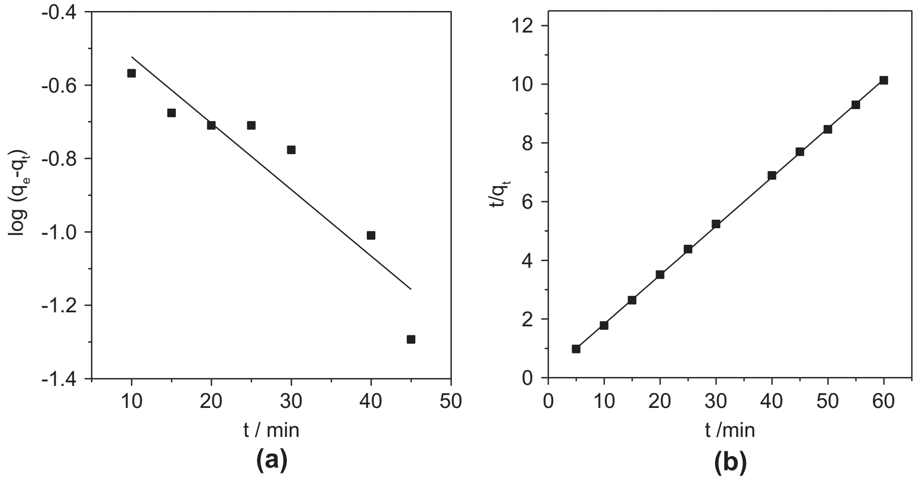

Fig. 6. (a) Pseudo-first-order kinetic and (b) pseudo-second-order kinetic for the adsorption of CV using AS.

Table 6
The parameters of the two kinetic models for dyes adsorption onto AS

c_0 (mg/L)	Pseudo-first-order model			Pseudo-second-order model		
	k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 ($\text{mg g}^{-1}\text{min}^{-1}$)	q_e (mg g^{-1})	R^2
200	0.04145	0.4561	0.8488	0.1693	5.9988	0.9998

indicated that the adsorption of CV onto AS followed pseudo-second-order kinetics. In addition, the q_e value in the pseudo-second-order model was calculated as 5.9988 mg g^{-1}, close to the experimental q_e value of 5.92 mg g^{-1}, illustrating that chemical adsorption was the rate-controlling step (see Table 6).

4. Conclusions

Adsorption equilibrium of CV onto AS has been investigated in detail, in an attempt to optimize and discuss the linear and interaction effects of process parameters including temperature, adsorbent dosage, contact time, and agitation speed on the percentage color removal of CV. A quadratic polynomial equation was established to predict the percentage color removal of CV by RSM. F-test and P values were used for examining the significance of each factor and their mutual interactions on the percentage color removal. The optimum conditions for the removal of CV by AS were found to be, a temperature of 33℃, adsorbent dosage of 23.3 g/L, contact time of 64 min, and agitate speed of 230 rpm. The suitable operation pH was found to be higher than 6.0. Furthermore, the experimental data fitted well with Langmuir isotherm model and the maximum adsorption capacity was calculated to be 40 mg g^{-1}. The kinetic studies indicated the adsorption process could be described with pseudo-second-order model very well. The results of this investigation supported the view of AS as an adsorbent material for CV removal. It should be worthy for the new application of AS and a new process design for CV removal from its effluent.

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