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Adsorptive removal of Cu^{2+} and direct sky blue 5B from aqueous solutions by acid treated tea waste—application of response surface methodology

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ABSTRACT

A low-cost adsorbent, tea waste was activated by nitric acid and adsorption of Cu^{2+} and direct sky blue 5B from aqueous solution was investigated. Response surface methodology (RSM) was used to study the adsorption process. The RSM results showed that temperature and concentration are major factors to modelling Cu^{2+} and direct sky blue 5B adsorption, respectively. Higher temperature has a positive effect on the adsorption of Cu^{2+} and direct sky blue 5B. Under the same temperature, the adsorption capacity was increased along with the concentration till maximum is attained both for Cu^{2+} and direct sky blue 5B. The optimum condition of the RSM for Cu^{2+} was determined as following: pH 4.5, 45°C, concentration of 1.5×10^{-2} mol/L; for direct sky blue 5B, the optimal condition were pH 6.0, 25°C, 1.5×10^{-2} mol/L. The equilibrium data during adsorption were modeled to Langmuir and Freundlich isotherms for Cu^{2+}. For direct sky blue 5B, the equilibrium data were well presented by Freundlich isotherms. The maximum adsorption capacities were determined at 59.88 mg/g for Cu^{2+}, 58.27 mg/g for direct sky blue 5B. The kinetic data fit to pseudo-second-order equation well with correlation coefficients larger than 0.99. The results strongly support that tea waste can be used as an economic and excellent adsorbent for the removal of Cu^{2+} and direct sky blue 5B from contaminated water.

Keywords: Tea waste; Adsorption; Copper; Response surface methodology; Isotherm; Kinetics

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1. Introduction

Heavy metals and dyes in wastewater, generated from textile and paper industries pose great threat to aquatic organisms and human beings according their accumulations [1–4]. Many heavy metals are well-known environmental toxins and carcinogenic and mutagenic even at low concentration [5,6]. Cu is a kind of trace elements which is necessary to human being. It can participate in body metabolism, but excessive accumulation may deteriorate body function [7]. In addition, strong color holding trend of the dyes lead to difficulty treatment following conventional removal processes with high hydrolyzing tendency and greater tinctorial value [8–10]. Direct sky blue 5B is a typical azo dye, commonly found in considerable amounts in printing waste water. It includes a chromophoric azo group (–N=N–) attaching to benzene or naphthalene derivatives. It is mainly used for cotton, viscose and other cellulose fiber staining, also applied as a paper and biological dye, used in film coloring and matching ink. The wastewaters containing direct sky blue 5B is one of the key sources of esthetic pollution, eutrophication, and perturbations in aquatic life [1]. Furthermore, the transmission of light could be interfered by dyes, and the biological metabolism processes could also be impacted, leaving the destruction of aquatic communities present in ecosystem [11].

Currently, many technologies are under development to remove many heavy metals and dye-contaminants from aquatic environments. For example, nanofiltration, ion-exchange, adsorption, membrane, electrochemical precipitation, electrocoagulation, and flotation are all examined in their efficacy to remove such environmental toxins [10,12,13]. Among them, adsorption is a well-established and

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powerful practice for the removal of heavy metals and dyes pollutants from wastewater with the advantages of simplicity and high-efficiency characteristics [14–18]. Thousands of adsorbents were used to remove heavy metals [8,19–21] or dyes [10,11,22,23]. Among thousands of adsorbents, activated carbon has shown to be effective for the removal of heavy metals and dyes. However, the high cost prevents the application of activated carbon for wastewaters treatment [24]. Agricultural waste and its industrial by-products have been massively investigated to remove the heavy metals and dyes because of its abundance and low cost [25–31]. Tea is consumed commonly in the whole word, especially in China. Tea waste, with its unique structure and physicochemical properties, has been widely used to remove heavy metals and dyes from aqueous solutions [20,24,32]. It has been reported that the acid adsorption increase the adsorption capacity, with surface oxides such as carbonyl, carboxyl, phenolic hydroxyl, lactone and quinine groups after acid treatment [33].

The response surface methodology (RSM) is a statistical technique for designing experiments, building models, evaluating the effects of several factors, and searching optimum conditions for desirable responses and reducing the number of experiments. RSM has been applied to optimize the adsorption process for many wastes [34–36].

Combined the low cost of tea waste and high-efficiency of acid adsorption, the adsorption performance of tea waste modified by nitric acid for the removal of Cu^{2+} and direct sky blue 5B from aqueous solutions was investigated. The RSM was used to investigate the adsorption properties of Cu^{2+} and direct sky blue 5B onto tea waste. Equilibrium isotherm data fit to Langmuir and Freundlich equations, constants of isotherm equations were determined. In addition, the pseudo-first and pseudo-second-order kinetic models were applied to study the adsorption kinetics of Cu^{2+} and direct sky blue 5B and quantify the extent of uptake in adsorption kinetics.

2. Materials and methods

2.1. Raw tea waste and modified tea waste

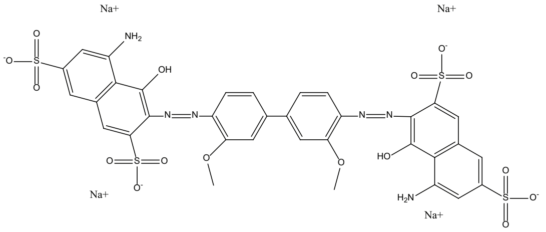
The tea waste used in this work was collected from organic laboratory after removal of caffeine. After grinding, sieving, 22–40 mesh (0.75–0.45 mm) tea dust was added to the distilled water and heated to boiling to remove all dirt particles. After cooling to room temperature, tea dust was rinsed in distilled water several times till no color was observed. The resulting tea dust then was transferred to the oven and dried at 80°C for 24 h, resulted raw tea waste (RTW).

Approximately, 20 g RTW was placed in 250 mL Erlenmeyer flasks, and 200 mL nitric acid (1 mol/L) was added into the flask, treated in room temperature for 30 min. Ultrasonic treatment was applied for 20 min in a CNC ultrasonic cleaner at 25°C with stirring by a glass rod. Distilled water was used to wash several times until pH reaches 7.0. Final product was derived after drying at 80°C for 24 h, resulting modified tea waste (MTW).

2.2. Chemicals

Cu^{2+} stock solution was prepared by dissolving 2.4555 g of $Cu(NO_3)_2·3H_2O$ in 500 mL distilled water, and Cu^{2+} concentration was determined with standard zinc and EDTA by residual titration. Direct sky blue 5B stock solution was obtained by dissolving 0.5 g of direct sky blue 5B in 1,000 mL distilled water. The standard curve of absorbance (598 nm) to concentration was as follows: $A = 0.0171C + 0.0027$, $R^2 = 0.9998$. The test concentrations were obtained by diluting stock solution to different concentrations. The pH of each solution was adjusted to the required value with diluted or concentrated HCl and NaOH.

$Cu(NO_3)_2·3H_2O$ and direct sky blue 5B were obtained from Aladdin, AR. Other chemicals were also AR. The molecular structure of direct sky blue 5B is as following:



2.3. Equilibrium studies

To investigate the influence of pH on Cu^{2+} and direct sky blue 5B adsorption by RTW and MTW, the adsorption experiments were performed in 250 mL Erlenmeyer flasks containing different concentration of Cu^{2+} and direct sky blue 5B solutions and with different amount of adsorbent. The adsorption experiments were carried out at ambient temperature (25°C ± 2°C) using 20 mL of the Cu^{2+} and dye solution and 0.05 g of the adsorbent. The flasks were placed in a thermostatic water bath shaker for 24 h till equilibrium was reached. After the adsorption, the concentrations of the Cu^{2+} and dye in the residual solutions were measured by residual titration and UV–Vis spectrophotometer.

The amount of adsorption at equilibrium, Q_e (mg/g) was calculated using the following equation [37]:

$$Q_e = (C_0 - C_e)V / m \tag{1}$$

where C_0 and C_e (mg/L) denote initial concentration and concentration of the adsorbate after time t (min), V is the volume of the adsorbate solution (L), m is the weight of the adsorbent used (g). The percentage removal of the adsorbate was calculated using the following equation:

$$\text{Removal percentage }(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

Based on the equilibrium studies, the influence of pH, temperature and the initial concentration of Cu^{2+} or dye was determined through a central composite design (CCD) of RSM.

2.4. Kinetic studies

The procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals. The concentrations of the Cu^{2+} and dye in the residual solutions were measured by residual titration and UV–Vis spectrophotometer. All the kinetic experiments were carried out at optimized pH from 2.3. The amount of sorption at time t, Q_t (mg/g) was calculated by the following equation [38]:

$$Q_t = (C_0 - C_t)V / m \quad (3)$$

where C_t (mg/L) is the liquid-phase concentration of Cu^{2+} or dye at any time.

2.5. Analysis for the adsorbent

The surface structure of adsorbents was observed by the scanning electron microscopy (SEM). Functional groups of adsorbent samples were determined by Fourier transform infrared spectroscopy (FTIR).

2.6. Studies on pH at zero point of charge

To determine pH_{zpc}, 0.1 M KNO_3 was prepared and its pH was adjusted in the range of 2–10 by adding NaOH or HCl. Then 50 mL of 0.1 M KNO_3 was put in 10 different flasks and then 200 ± 1 mg of RTW and MTW were added to these solutions [39]. The flasks were kept for 48 h at 25°C in thermostatic oscillator and final pH of the solution was measured by using pH meter. The pH_{zpc} (pH at zero point of charge) was determined by $\Delta pH - pH_i$ graphs.

3. Results and discussion

3.1. FT-IR analysis

FTIR spectra of RTW, MTW are shown in Fig. 1. In the FTIR spectrum, the broad and intense absorption peaks observed around 3,500–3,300 cm^{-1} correspond to the O–H stretching vibrations due to inter- and intra-molecular hydrogen bonding. The peak at 2,920–2,930 cm^{-1} is attributed to the symmetric and asymmetric C–H stretching vibration. The peak at 1,700–1,710 cm^{-1} is due to asymmetric stretching vibrations of C=O and the peak observed at 1,615–1,620 cm^{-1} can be assigned to C=C stretching which may be corresponding to the sugar rings of lignin. The other prominent peaks are due to C–O (1,020 cm^{-1}, respectively) groups. Overall, FTIR analysis revealed the chemical nature of the absorbent. Based on FTIR spectra, the chemical structure of the tea waste remains almost the same after the modification and adsorption. Weng et al. [44] also verified that the chemical nature of wasted black tea powder remains almost the same after Cu^{2+} adsorption.

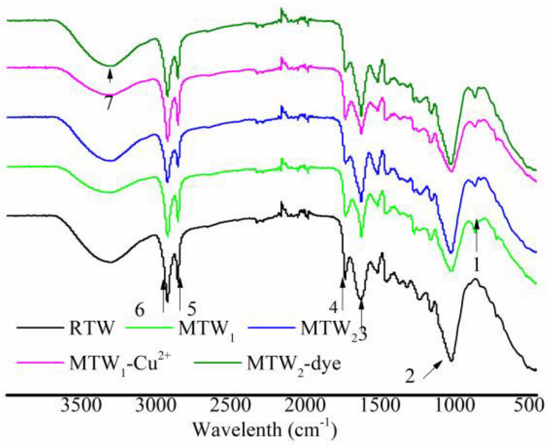


Fig. 1. FTIR spectra of RTW and MTW.

3.2. Scanning electron microscopy analysis

Scanning electron micrographs (Fig. 2) show that surface of RTW and MTW were not smooth and pores extensively existed (Figs. 2(a) and (b)). The magnification of SEM was 500×. Rough surface and extensively distributed pores can offer greater surface area and extra binding sites for Cu^{2+} or direct sky blue 5B. The surface modified absorbent after adsorption (Figs. 2(c) and (d)) showed that the surface of MTW was covered with Cu^{2+} or direct sky blue 5B.

3.3. pH_{zpc} of the adsorbent

Zero point of charges (pH_{zpc}) were determined for the RTW and MTW. The pH_{zpc} is an important property and it indicates the electrical neutrality of the adsorbent and surface at a special value of pH. The graph of pH_i vs. ΔpH was plotted as shown in Fig. 3. The intersections of the curves with the straight line (ΔpH = 0) are known as the end points of the pH_{zpc}, and these values are 6.1 and 2.6 for RTW and MTW, respectively.

3.4. Effect of different physico-chemical parameters

3.4.1. Influence of pH

The effects of pH of the suspending medium on Cu^{2+} and direct sky blue 5B adsorption were studied by performing equilibrium adsorption experiments at different pH values. The results are illustrated in Fig. 4. The effect of pH on Cu^{2+} adsorption was examined in the pH range 2.5–6.0. For both

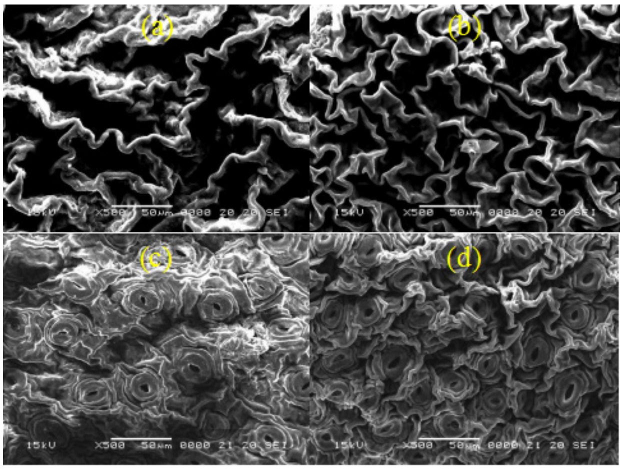


Fig. 2. SEM images of RTW, MTW, before and after Cu^{2+} or direct sky blue 5B adsorption. (a) RTW, (b) MTW, (c) MTW-Cu^{2+}, and (d) MTW-dye.

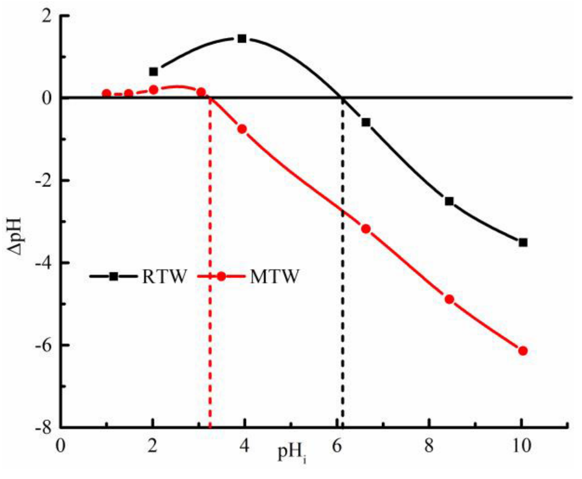


Fig. 3. Plot for determination of point of zero charge of raw tea and modified tea waste.

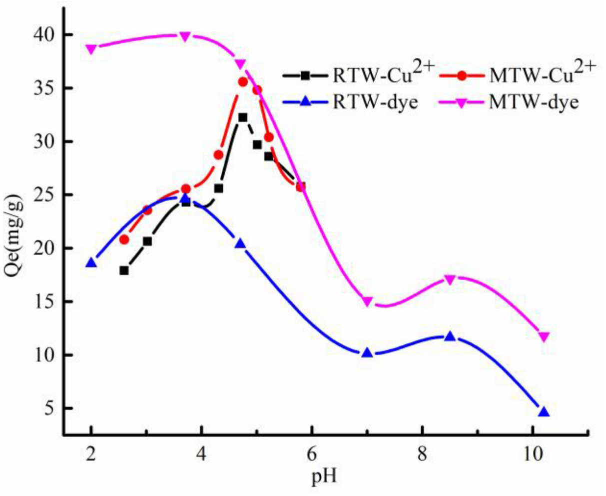


Fig. 4. Effect of pH on Cu^{2+} and direct sky blue 5B adsorption.

RTW and MTW, the uptake efficiency gradually increased as the pH ranging from 2.5 to 4.7. The concentration of H^+ ion is high at low pH, causing a competition for vacant adsorbent site between the H^+ ion and Cu^{2+} cations leading to the low removal efficiency. pH = 4.7, the adsorption capacity was peaking at 35.6 mg/g for MTW and 32.2 mg/g for RTW. Hence the optimum pH range for the removal of Cu^{2+} was found to be 4.7. While pH > 4.7, a portion of Cu^{2+} ions may be hydrolyzed into $Cu(OH)^+$ and $Cu(OH)_2$. $Cu(OH)_2$ was formed as sediment, which will affect its adsorption on tea residue.

It was observed that pH has significant influence on the direct sky blue 5B adsorption process. Direct sky blue 5B is an anionic dye, and the negative charged ions existed in aqueous solution. As a charged species, the degree of its adsorption onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is modulated by the solution pH [40]. As shown in Fig. 4, the equilibrium adsorption capacity was increased from pH = 2–4 onto RTW, while the equilibrium adsorption capacity had almost no change from pH = 2–4 onto MTW. Then the equilibrium adsorption capacity decreased significantly over the initial pH ranges of 4–10. At lower pH (lower than the pH_{zpc}), the positively charged adsorbent surface was favorable for the adsorption of the anionic dye direct sky blue 5B. Because of ionization of MTW functional groups, an obviously strong electrostatic attraction existed between the positively charged adsorbent surface and the negatively charged anionic direct sky blue 5B. Thus, less adsorption occurred at higher pH. This may also be due to the fact that the excessive anionic ions on the surface of the MTW competed with anionic ions of direct sky blue 5B for the adsorption sites, resulting in a reduced adsorption capacity due to the electrostatic interaction.

3.4.2. Interaction among factors influencing Cu^{2+} adsorption

The influences of different parameters such as of initial pH (A), adsorbent temperature (B) and Cu^{2+} concentration (C) on Cu^{2+} ions adsorption capacity by MTW were investigated and optimized. Optimization of Cu^{2+} ions adsorption capacity by RSM [41] and CCD was employed to evaluate the interaction among the significant variables and to determine their optimal values. The experimental conditions for runs and the corresponding responses including observed and predicted response along with experimental values of response in terms of adsorption capacity of Cu^{2+} ions are presented in Table 1.

Final empirical model for Cu^{2+} adsorption capacity (Q_e mg/g) by MTW in terms of actual factors was expressed by the following equation:

$$Q_e = 37.52 - 0.43 \times A + 4.28 \times B + 2.31 \times C - 1.55 \times AB - 0.67 \times AC - 0.16 \times BC - 10.96 \times A^2 + 0.61 \times B^2 + 0.095 \times C^2 \qquad (4)$$

The equation confirms more contribution and positive influence of variable C as main effect and the interaction among variable B and C. The equation also reveals that variable A has a negative trend on response, which corresponds to the results of section 3.4.1. The optimum condition of the RSM for Cu^{2+} was pH 4.5, 45°C, 1.5×10^{-2} mol/L, with the adsorption capacity of 59.88 mg/g.

The main interaction and quadratic effects were evaluated in this design. To find the most important interaction, analysis of variance (ANOVA) at 95% confidence level was calculated using Design-Expert software (Table 2). Larger F-values and lower probability values (p-values) revealed the significance and suitability of quadratic model, with high F-value (12.18) and low p-value (0.0003).

The 3D graphs correspond to Cu^{2+} ions adsorption capacity, which depict their variation against the variables were plotted at optimum values of other factors and their curvatures are proportional with presence of significance interaction among the variables. Fig. 5 demonstrates that Cu^{2+} ions adsorption capacity is strongly affected by the pH and Cu^{2+}concentration. The higher value of adsorption capacity at lower pH especially at high concentration of Cu^{2+} was found. As shown in Fig. 5, the adsorption capacity of Cu^{2+} ions by the MTW increase sharply from 15.6 to 37.6 mg/g along with the pH range of 2.0 to 4.0, followed by a slow decrease from pH 4.0 to 6.0. As pH increased, the deprotonation of the acidic groups on the MTW surface is enhanced and the negative charges increase, promoting the adsorption of positively charged Cu^{2+} ions by electrostatic

Table 1
CCD with actual responses for Cu^{2+} adsorption capacity (Q_e mg/g) by MTW with predicted responses after analysis

Runs	Factors			Q_e (mg/g)		Residual	Cook's distance
	pH	T (°C)	C (mol/L $\times 10^{-2}$)	Observed responses	Predicted responses		
1	4.0	35	1.0	37.59	37.52	0.07	0.00
2	6.0	25	0.5	24.49	23.18	1.31	0.05
3	4.0	35	0.16	36.52	33.90	2.62	0.14
4	4.0	35	1.0	37.59	37.52	0.07	0.00
5	4.0	35	1.84	36.68	41.38	–5.00	0.51
6	2.0	25	1.5	23.57	24.15	–0.58	0.01
7	7.36	35	1.0	0	7.25	–7.25	1.06
8	4.0	35	1.0	37.59	37.52	0.07	0.00
9	6.0	25	1.5	32.78	26.78	6.00	1.13
10	4.0	35	1.0	37.59	37.52	0.07	0.00
11	2.0	45	1.5	35.87	35.49	0.38	0.00
12	4.0	18.18	1.0	30.25	32.07	–1.82	0.07
13	6.0	45	0.5	31.21	28.94	2.27	0.16
14	0.64	35	1.0	10.68	5.80	4.87	0.48
15	2.0	25	0.5	15.57	17.87	–2.30	0.17
16	4.0	35	1.0	37.59	37.52	0.07	0.00
17	6.0	45	1.5	35.90	31.91	3.99	0.50
18	4.0	35	1.0	37.59	37.52	0.07	0.00
19	4.0	51.82	1.0	45.88	46.45	–0.57	0.01
20	2.0	45	0.5	25.53	29.84	–4.31	0.59

Table 2
ANOVA for response surface quadratic model on Cu^{2+} adsorption capacity by MTW

Source	Sum of squares	d*f*	Mean squares	*F*-value	*p*-value probability > *F*
Model	2,136.61	9	237.40	12.18	0.0003
A-pH	2.54	1	2.54	0.13	0.7254
B-temperature	249.62	1	249.62	12.80	0.0050
C-concentration	73.07	1	73.07	3.75	0.0816
AB	19.28	1	19.28	0.99	0.3434
AC	3.59	1	3.59	0.18	0.6769
BC	0.20	1	0.20	0.01	0.9216
A^2	1,730.60	1	1,730.60	88.77	<0.0001
B^2	5.42	1	5.42	0.28	0.6094
C^2	0.13	1	0.13	6.73×10^{-3}	0.9362
Residual	194.96	10	19.50		
Lack of fit	194.96	5	38.99		
Pure error	0.00	5	0.00		
Corrected total	2,331.57	19			

attraction [42]. While pH > 4.0, a portion of Cu^{2+} ions may be hydrolyzed into $Cu(OH)^+$ and $Cu(OH)_2$. While, the adsorption capacity of Cu^{2+} ions by the MTW increase along with temperature and initial concentration of Cu^{2+}.

3.4.3. Interaction among factors influencing dye adsorption

It is well known that the adsorption capacity for dye is always limited by pH, temperature and its initial concentration. Based on the CCD analysis (Table 3), a model (Eq. (5)) was derived that could relate adsorption capacity for direct sky blue 5B as a measured output in response to the independent input variables.

$$\begin{aligned} Q_e = {} & 60.11 - 9.08 \times A + 15.63 \times B + 25.42 \times C - 3.12 \times AB \\ & - 5.73 \times AC + 10.32 \times BC - 9.83 \times A^2 + 4.11 \times B^2 \\ & - 1.43 \times C^2 \end{aligned} \tag{5}$$

The optimum condition of the RSM for direct sky blue 5B was pH 6.0, 25°C, 1.5×10^{-2} mol/L, with the adsorption

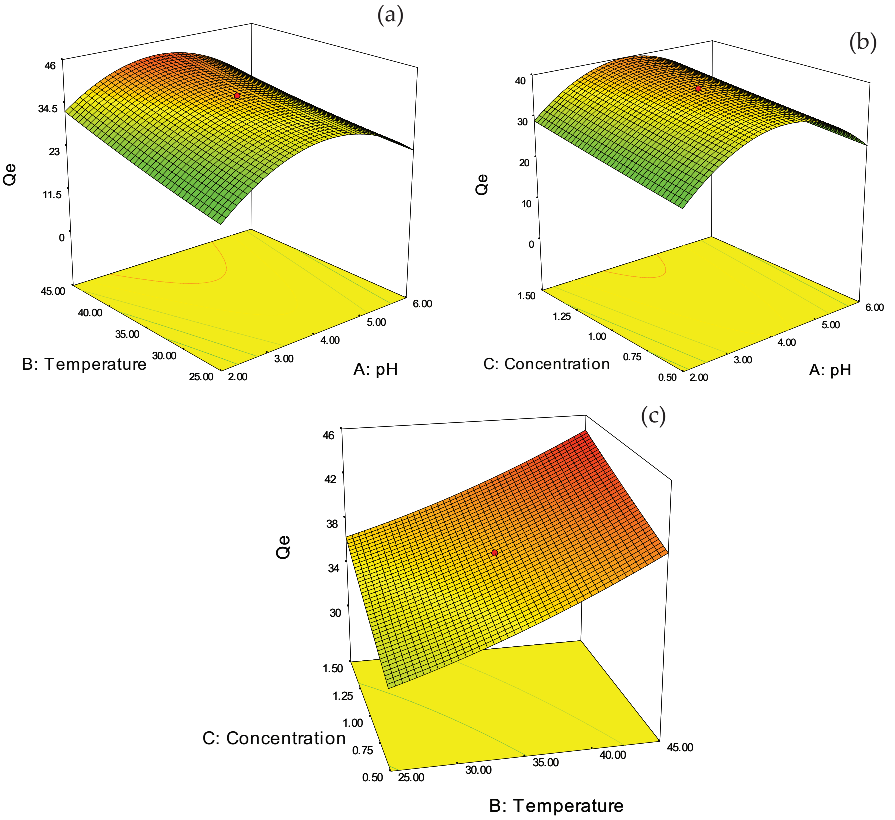


Fig. 5. 3D surface plot: (a) interaction between temperature and pH, (b) interaction between Cu^{2+} ions concentration and pH, and (c) interaction between temperature and Cu^{2+} ions concentration.

Table 3
CCD with actual responses for direct sky blue 5B adsorption capacity (Q_e mg/g) by MTW with predicted responses after analysis

Runs	Factors			Q_e (mg/g)		Residual	Cook's distance
	pH	T (°C)	C (mol/L × 10^{-2})	Observed responses	Predicted responses		
1	4.0	35	1.0	61.49	60.11	1.38	0.00
2	6.0	25	0.5	83.11	64.11	19	0.57
3	4.0	35	0.16	10.34	13.31	–2.97	0.01
4	4.0	35	1.0	62.44	60.11	2.33	0.00
5	4.0	35	1.84	80.52	86.39	–5.87	0.56
6	2.0	25	1.5	59.11	60.11	–1.00	0.00
7	7.36	35	1.0	21.94	26.36	–4.42	0.03
8	4.0	35	1.0	10.28	47.56	–37.28	1.41
9	6.0	25	1.5	146.67	122.24	24.43	0.94
10	4.0	35	1.0	44.67	40.74	3.93	0.02
11	2.0	45	1.5	42.91	22.46	20.54	0.66
12	4.0	18.18	1.0	12.14	21.99	–9.85	0.15
13	6.0	45	0.5	33.70	17.03	16.67	0.28
14	0.64	35	1.0	90.30	98.00	–7.70	0.06
15	2.0	25	0.5	32.54	45.45	–12.91	0.17
16	4.0	35	1.0	60.56	60.11	0.45	0.00
17	6.0	45	1.5	58.48	60.11	–1.63	0.00
18	4.0	35	1.0	49.95	39.31	10.64	0.18
19	4.0	51.82	1.0	81.17	98.81	–17.64	0.32
20	2.0	45	0.5	62.13	60.11	2.02	0.00

capacity of 58.27 mg/g. In this case, initial dye concentration and temperature were found to have significant effects with the coefficient 25.42 and 15.63, respectively. While pH has a negative effect on the dye adsorption, with a coefficient –9.08, the quadratic effect of initial dye concentration as well as the interaction effects between *AB*, *AC* and *BC* were considered as significant effects. There was a synergistic effect between initial dye concentration and temperature on dye adsorption, with the coefficient for the two factors being 10.32.

ANOVA was used to assess the significance of each variable in the model. For direct sky blue 5B adsorption capacity, the Model F-value of 4.65 implied that the model was significant as well (Table 4). According to ANOVA results, the values of Probability > *F* less than 0.05 imply that the model terms were significant. Probability > *F* indicates the probability that all the uncertainty in the results is caused by random error, and therefore the low probability values (0.0004) observed for responses indicate that obtained data are not random and the models are significant.

The 3D response surface plots were drawn to investigate the effects of three factors on the adsorption behavior by considering all the significant interactions in the CCD. Fig. 6 shows the interaction of temperature with pH, interaction of direct sky blue 5B concentration with pH, interaction of temperature with direct sky blue 5B concentration. In each graph, two factors were changed while keeping three remained factors at the middle level. As shown in Fig. 6, the adsorption capacity is obviously increased with increase of temperature and the initial concentration of direct sky blue 5B. The maximum adsorption capacity value was achieved when the two factors were kept at the highest point within the studied range. However, the adsorption capacity increases from 42.9 to 90.3 mg/g with increasing pH from 2.0 to 4.0.

3.5. Adsorption isotherms

In the present investigation, the equilibrium data were analyzed using the Langmuir [45] and Freundlich [46] isotherm expression given by the following equations, respectively.

Langmuir:

$$Q_e = q_{m,L} b_L C_e / (1 + b_L C_e) \tag{6}$$

Freundlich:

$$Q_e = K_F C_e^{1/n} \tag{7}$$

where Q_e is the adsorption capacity (mg/g) at equilibrium of Cu^{2+} or direct sky blue 5B; $q_{m,L}$ is the maximal adsorption capacity (mg/g); C_e is the equilibrium concentration of Cu^{2+} or direct sky blue 5B in solution (mg/L); b_L is a binding constant (L/g); K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity of adsorbents.

The linearized forms of Langmuir and Freundlich equations can be written as follows:

$$\frac{1}{Q_e} = \frac{1}{q_{m,L} b_L} \frac{1}{C_e} + \frac{1}{q_{m,L}} \tag{8}$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{9}$$

Table 5 shows the adsorption equilibrium data fitted to Langmuir equation (Eq. (8)) and Freundlich equation (Eq. (9)) isotherm expression, respectively. It is evident from Table 5 that the equilibrium data were well represented by the Freundlich isotherm equation and the Langmuir equation for Cu^{2+}. The surface of the tea waste was anisotropic, containing N and O atoms on its surface which could complex with heavy metal ions. Cu^{2+} complexed easily with N, O on the surface of the tea waste. The adsorption of Cu^{2+} fit well for the Langmuir and the Freundlich isotherm.

While for the direct sky blue 5B, the equilibrium data were followed well Freundlich isotherm. Compared with Cu^{2+}, the structure of direct sky blue 5B was complex with

Table 4
ANOVA for response surface quadratic model on direct sky blue 5B adsorption capacity by MTW

Source	Sum of squares	d*f*	Mean squares	*F*-value	*p*-value probability > *F*
Model	16,258.73	9	1,806.53	4.65	0.0004
A-pH	1,125.56	1	1,125.56	2.90	0.1196
B-temperature	3,334.26	1	3,334.26	8.58	0.0151
C-concentration	8,824.44	1	8,824.44	22.71	0.0008
AB	77.81	1	77.81	0.20	0.6640
AC	262.32	1	262.32	0.68	0.4304
BC	852.23	1	852.23	2.19	0.1694
A^2	1,393.84	1	1,393.84	3.59	0.0875
B^2	242.97	1	242.97	0.63	0.4474
C^2	29.57	1	29.57	0.076	0.7883
Residual	3,885.16	10	388.52		
Lack of fit	3,871.99	5	774.40	293.94	<0.0001
Pure error	13.17	5	2.63		
Corrected total	20,143.89	19			

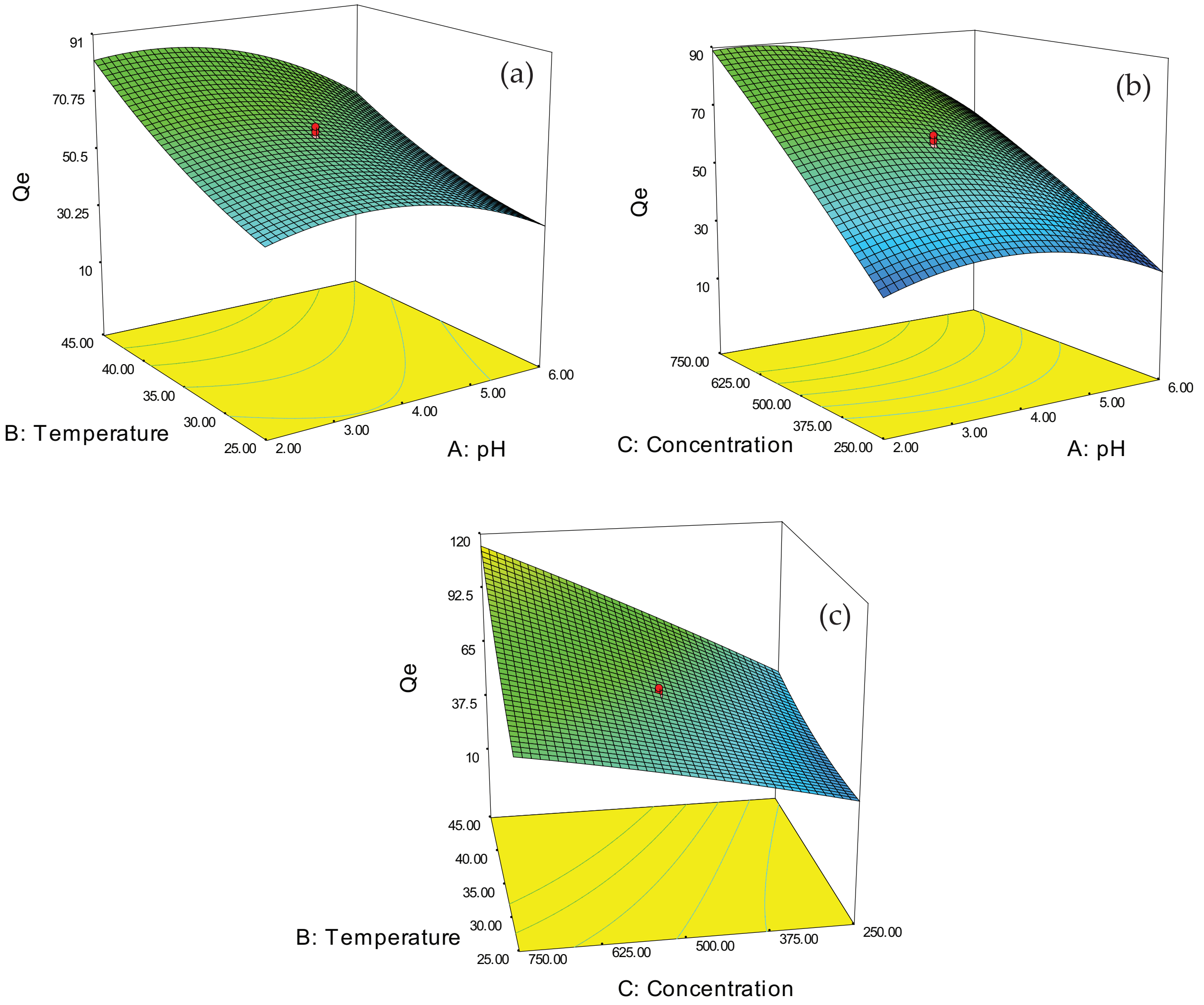


Fig. 6. 3D surface plot: (a) interaction between temperature and pH, (b) interaction between direct sky blue 5B concentration and pH, and (c) interaction between temperature and direct sky blue 5B concentration.

multiple functional groups. The interactions between tea waste and direct sky blue 5B may be more complicated, including hydrogen bond interaction, dipole–dipole interaction and van der Waals interaction.

The calculated Freundlich constants for Cu^{2+}, K_F are 5.88, 1.79, and 9.29 and n are 3.79, 2.17, and 4.35 at 25°C, 35°C, and 45°C, respectively. While for the direct sky blue 5B, K_F are 0.14, 2.50, and 3.13 and n are 0.97, 1.34, and 2.54 at 25°C, 35°C, and 45°C, respectively.

The best fit of equilibrium data of Cu^{2+} in the Langmuir isotherm expression was at 35°C, with high b_L (9.15) value shows. The adsorption capacity of MTW for Cu^{2+} increased along with temperature, with the highest adsorption capacity (59.88 mg/g) at 45°C. The adsorption capacity of acid treated tea waste was agree with that of NaOH treated black tea leaf [42], while less than the report by Albadarin et al. [43]. However, the adsorption process of direct sky blue 5B was not fitted the Langmuir isotherm equation. While, Nasuha et al. [40] indicated that the adsorption isotherm data of anionic dye methylene blue (MB) fitted well to Langmuir isotherm onto NaOH-modified rejected tea. Although MB and direct sky blue 5B are anionic dyes, they presented different adsorption behavior onto tea waste, when they were modified with different reagents.

3.6. Adsorption kinetics

In the present work, the kinetic data obtained from batch studies have been analyzed by pseudo-first-order and pseudo-second-order models. The pseudo-first-order and pseudo-second-order kinetic equations are expressed in the form as follows [37,47]:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{10}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{11}$$

where Q_e and Q_t are the amount of metal or direct sky blue 5B adsorbed per unit weight of adsorbent (mg/g) at equilibrium, and at time t, respectively; and k_1 and k_2 are the adsorption rate constants of pseudo-first-order and pseudo-second-order kinetic equations.

Table 5
Langmuir and Freundlich isotherm constants for adsorption of Cu^{2+} and direct sky blue 5B onto tea waste and modified tea waste in this work and compared with literature

Adsorbent	T (°C)	Isotherm model											
		Langmuir $Q_e = q_{m,L}b_LC_e/(1 + b_LC_e)$						Freundlich $Q_e = K_FC_e^{1/n}$					
		$q_{m,L}$ (mg/g)		b_L (L/g)		R^2		K_F		n		R^2	
		Cu^{2+}	Dye	Cu^{2+}	Dye	Cu^{2+}	Dye	Cu^{2+}	Dye	Cu^{2+}	Dye	Cu^{2+}	Dye
RTW	25	46.30		2.49		0.99		2.20	4.65	2.56	0.51	0.99	0.949
	35	41.67		5.71		0.98		4.78	0.40	3.44	0.91	0.98	0.999
	45	51.81		3.49		0.98		7.31	0.20	4.04	0.99	0.99	0.989
MTW	25	43.86		5.04		0.99		5.88	0.14	3.79	0.97	0.99	0.99
	35	45.45		9.15		0.98		1.79	2.50	2.17	1.34	0.99	0.99
	45	59.88		3.22		0.99		9.29	3.13	4.35	2.54	0.99	0.99
TW[a]	22	48		7.6		0.99		0.70		1.35		0.98	
TW[b]	20	77.31	130.5	15	271	0.96	0.95	2.49	28.02	1.49	1.56	0.98	0.91
OH-BTLP[c]	4	35.2		13.02		0.99							
	16	38.4		13.31		0.99							
	26	43.52		13.97		0.99							
	38	46.72		15.91		0.99							
RT[d]	30		147.0		47		0.99		3.15		2.19		0.98
	40		154.0		49		0.99		3.41		2.29		0.93
	50		156.0		60		0.99		3.69		2.45		0.94
PTP[e]	25		277.8[f]		83		0.99		33.93		1.96		0.97
			285.7[g]		99		0.99		39.06		2.00		0.96
			294.1[h]		138		0.99		47.95		2.05		0.96

[a] Tea waste for Cu^{2+} pH = 5–6 [26].
[b] Tea waste for Cu^{2+} pH = 4.5, for methylene blue pH = 7.0 [43].
[c] Black tea leaf powder washed with 0.1 mol/L NaOH for 1 h, for Cu^{2+} pH = 4.4 [44].
[d] Rejected tea for methylene blue pH = 6–7 [40].
[e] Pu-erh tea powder for methyl violet.
[f] 40 mesh.
[g] 200 mesh.
[h] Nano-particle [28].

The kinetic parameters calculated are shown in Table 6. The equilibrium sorption capacities determined by first and second order model were agreed with the experimentally determined equilibrium adsorption capacities. The pseudo-first-order rate constant k_1 of Cu^{2+} decreases with the temperature, and the same as k_1 of direct sky blue 5B. However, the pseudo-second-order rate constant k_2 of Cu^{2+} increases with the temperature, while k_2 of direct sky blue 5B decreases with the temperature.

From Table 6, the pseudo-first- and pseudo-second-order models fit the kinetic data with adequate accuracy ($R^2 > 0.97$). However, the experimental data demonstrated more agreement with the pseudo-second-order model and higher correlation coefficients than the pseudo-first-order model. This indicates that chemical adsorption was the main control process for the modified tea waste and the uptake capacity is proportional to the number of active sites.

3.7. Removal rate

Removal of Cu^{2+} and direct sky blue 5B at different initial concentration along with different dose of absorbent is presented in Fig. 7. For Cu^{2+} adsorption, the removal efficiency decreased along with the initial concentration when the absorbent (both RTW and MTW) dose was fixed. While at the same initial concentration of Cu^{2+}, the removal efficiency increased significantly with increasing absorbent amount. When the absorbent amount increased from 0.1 to 0.3 g, the removal percentage increased from 31.0% to 96.3% by MTW.

While for direct sky blue 5B, the removal rate showed different properties. When the dye was treated with RTW, the removal efficiency increased along with the initial concentration with fixed absorbents. Also, with the same initial concentration of direct sky blue 5B, the removal efficiency increased significantly, while at the high concentration, the removal efficiency reaches saturation gradually with the increase of absorbent.

The different adsorption properties of Cu^{2+} and direct sky blue 5B onto the tea waste possibly resulted from the adsorption force. The surface of the tea waste was anisotropic, containing N and O atoms on its surface which could complex with heavy metal ions. According to literature [44,48], the mechanism for the adsorption of Cu^{2+} on the

Table 6
Kinetic parameters for the removal of Cu^{2+} and direct sky blue 5B by tea waste and modified tea waste in this work and compared with literature

Adsorbent	T (°C)	Kinetics model											
		Pseudo-first-order $\ln(Q_e - Q_t) = lnQ_e - k_1 t$						Pseudo-second-order $t/q_t = 1/(k_2 Q_e^2) + t/Q_e$					
		$Q_{e,\text{cal}}$ (mg/g)		k_1 (1/min)		R^2		$Q_{e,\text{cal}}$ (mg/g)		k_2 (g/mg·min × 10^{-4})		R^2	
		Cu^{2+}	Dye	Cu^{2+}	Dye	Cu^{2+}	Dye	Cu^{2+}	Dye	Cu^{2+}	Dye	Cu^{2+}	Dye
RTW	25	22.65	35.52	0.0035	0.0013	0.95	0.92	29.21	53.08	2.10	1.09	0.99	0.99
	35	24.78	43.38	0.0029	0.0016	0.92	0.95	33.22	63.09	1.83	0.86	0.99	0.99
	45	25.79	49.02	0.0020	0.0016	0.90	0.98	38.01	69.83	1.70	0.77	0.99	0.99
MTW	25	29.08	60.34	0.0028	0.0015	0.98	0.99	37.11	80.65	1.36	0.49	0.99	0.99
	35	29.67	71.52	0.0025	0.0017	0.97	0.99	40.02	93.81	1.45	0.44	0.99	0.99
	45	28.02	84.86	0.0019	0.0022	0.97	0.99	43.29	106.16	1.58	0.41	0.99	0.99
TW[a]	22							19[b]		0.0133		1.00	
								14[c]		0.0170		1.00	
								8[d]		0.0427		1.00	
								4[e]		0.1268		1.00	
TW[f]	20	55.68	109.4	0.221	0.407	0.90	0.99	59.26	112.8	0.005	0.007	0.97	1.00
RT[g]	30		18.6[h]		0.006		0.96		20.8		0.005		0.99
			34.9[i]		0.004		0.94		40.5		0.002		0.99
			69.9[j]		0.005		0.94		80		0.001		0.99
			99.9[k]		0.004		0.97		116		0.001		0.99
			117[l]		0.027		0.96		128		0.001		0.99
			134[m]		0.003		0.97		145		0.001		0.99
PTP[n]	25				0.0135[o]		0.97				0.383		0.99
					0.0194[p]		0.99				0.261		0.99
					0.0194[q]		0.99				0.176		0.99

[a] Tea waste for Cu^{2+} pH = 5–6.
[b] Initial concentration of Cu^{2+} 200 mg/L.
[c] Initial concentration of Cu^{2+} 100 mg/L.
[d] Initial concentration of Cu^{2+} 50 mg/L.
[e] Initial concentration of Cu^{2+} 25 mg/L [26].
[f] Tea waste for Cu^{2+} pH = 4.5, for methylene blue(MB) pH = 7.0 [32].
[g] Rejected tea for MB pH = 6–7.
[h] Initial concentration of MB 50 mg/L.
[i] Initial concentration of MB 100 mg/L.
[j] Initial concentration of MB 200 mg/L.
[k] Initial concentration of MB 300 mg/L.
[l] Initial concentration of MB 400 mg/L.
[m] Initial concentration of MB 500 mg/L [40].
[n] Pu-erh tea powder for methyl violet.
[o] 40 mesh.
[p] 200 mesh.
[q] Nano-particle [28].

nitric acid modified TW may include complexation, chelation and electrostatic interaction. For direct sky blue 5B, the structure was complex with multiple functional groups. The interactions between tea waste and direct sky blue 5B may be more complicated, including hydrogen bond interaction, dipole–dipole interaction and van der Waals interaction.

4. Conclusion

The nitric acid modified tea waste was found to be an effective and low-cost alternative in the detoxification of Cu^{2+} and direct sky blue 5B contaminated solutions. The pH, temperature and initial concentration of the adsorbate significantly affected the adsorption efficiency for Cu^{2+} and direct sky blue 5B adsorption based on the results of RSM. Higher temperature has a positive effect on the adsorption of Cu^{2+} and direct sky blue 5B. Under the same temperature, the adsorption capacity was increased along with the concentration till maximum is attained both for Cu^{2+} and direct sky blue 5B. The optimum condition of the RSM for Cu^{2+} was determined as following: pH 4.5, 45°C, concentration of 1.5×10^{-2} mol/L; for direct sky blue 5B, the optimal condition were pH 6.0, 25°C, 1.5×10^{-2} mol/L. The equilibrium data for Cu^{2+} were well represented by both the Langmuir and Freundlich isotherms. While for the direct sky blue 5B, the equilibrium adsorption fit well with the Freundlich isotherm. The maximum adsorption

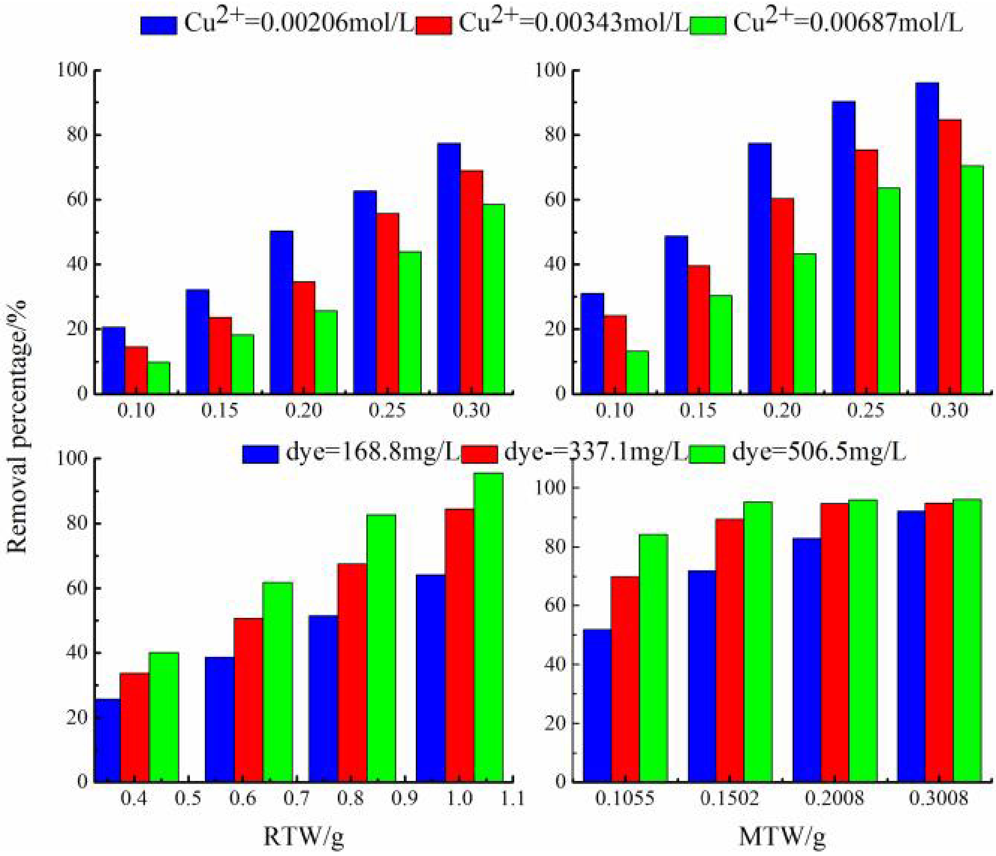


Fig. 7. Removal of Cu^{2+} and direct sky blue 5B at different initial concentration along with different dose of absorbent.

capacities were determined at 59.88 mg/g for Cu^{2+}, 58.27 mg/g for direct sky blue 5B. The adsorption dynamics fit the pseudo-second-order kinetic model, with correlation coefficients larger than 0.99. The mechanism for the adsorption of Cu^{2+} on the nitric acid modified TW may include complexation, chelation and electrostatic interaction. For direct sky blue 5B, the interactions included hydrogen bond interaction, dipole–dipole interaction and van der Waals interaction. It was confirmed that modification of TW is capable of improving its adsorption capacity for Cu^{2+} and direct sky blue 5B and can serve as cheap non-conventional adsorbent in wastewater treatment.

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