



Fast removal of methylene blue from aqueous solution by adsorption onto chitosan-g-poly (acrylic acid)/attapulgite composite

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ABSTRACT

Batch adsorption experiments were carried out for the removal of methylene blue (MB) cationic dye from aqueous solution using chitosan-g-poly (acrylic acid)/attapulgite composites (CTS-g-PAA/APT) as adsorbent. The effects of attapulgite (APT) content, initial pH value of the dye solution and temperature on adsorption were investigated. Results showed that APT content of composites had some influence on adsorption capacities, and introducing a small amount of APT could improve adsorption capacity of chitosan-g-poly (acrylic acid) (CTS-g-PAA) to a certain extent. Results from kinetic experimental data showed that the adsorption rate of MB on CTS-g-PAA and CTS-g-PAA/APT with 30% of APT was fast, and more than 90% of the maximum adsorption capacities for MB were achieved within the initial 15 min. The adsorption behaviors of CTS-g-PAA and CTS-g-PAA/APT showed that the adsorption kinetics and isotherms were in good agreement with a pseudo-second-order equation and the Langmuir equation, and the maximum adsorption capacities reached 1873 and 1848 mg/g for CTS-g-PAA and CTS-g-PAA/APT, respectively. The discussion results of the desorption studies implied that CTS-g-PAA and CTS-g-PAA/APT can be used as promising adsorbents for the removal of MB from wastewater.

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1. Introduction

Wastewaters from industries like textile, dyeing, printing, cosmetics, food coloring, papermaking, etc. are the major contributors of colored effluents [1]. There are more than 100,000 commercially available dyes with over 7×10^5 tons of dyes produced annually [2]. It is estimated that 2% of dyes produced annually are discharged in effluent from manufacturing operations, while 10% was discharged from textile and associated industries [3]. Discharging of dyes into water resources even in a small amount can affect the aquatic life and food web. Dyes can also cause allergic dermatitis and skin irritation. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms and humans [4–6]. Methylene blue (MB) is the most commonly used substance for dyeing cotton, wood and silk. MB can cause eye burns which may be responsible for permanent injury to the eyes of humans and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [7]. Therefore, the removal of MB from waste effluents becomes environmentally important.

Most of the dyes are stable to photodegradation and biodegradation [8–10]. Thus, colored wastewater poses a challenge to the conventional wastewater treatment techniques. Thus far, many methods such as coagulation and flocculation [11], membrane separation [12], oxidation or ozonation [13,14], electro-coagulation [15] and adsorption [16] have been utilized for removing dyes. Among them, adsorption has been found to be an effective, cheap and potential technique for removing dyes or other infectant [17], and many different types of adsorbents were developed and used for the effective removal of color from aqueous effluent. In recent years, natural polymeric materials have drawn considerable attention because they are renewable, biodegradable, non-toxic and potential as an environmentally friendly material [18]. Chitosan (CTS) is the *N*-deacetylated derivative of chitin and the second most plentiful natural biopolymer. As a well-known sorbent, CTS is widely used for the removal of heavy metals and dyes [19–21]. However, CTS can only adsorb very small amounts of cationic dyes because it is a natural cationic polysaccharide. Moreover, the relatively high market cost and low specific gravity also limited its practical operation. Recently, clays such as montmorillonite [22–25], attapulgite [26,27], kaolin [28] and mica [29] are gaining interest for application as adsorbents in wastewater treatment due to their low cost. However, the dispersion and suspension abilities of clay in aqueous solution need to be improved for practical operation. Therefore, several attempts have been made to develop more effective adsorbents.

Hydrogels are formed of three-dimensional crosslinked polymer networks of flexible chains, which are able to absorb and retain water

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and solute molecules. The higher water content and porous network structures allow solute diffusing through the hydrogel structure [30]. As hydrogels possess ionic functional groups such as carboxylic acid, amine, hydroxyl and sulfonic acid groups, they can absorb and trap metal ions [31,32] or cationic dyes such as MB [33] from wastewater. Therefore, the hydrogels may be used as an alternative adsorbent for the removal of cationic dyes from aqueous solution. Nevertheless, as to our knowledge, the study on MB dye adsorption using CTS-g-PAA/APT composites has rarely been reported. Therefore, on the basis of our previous work about the preparation and water absorbency of CTS-g-PAA/APT composites [34], the adsorption capacities of the composites for MB were studied in this paper. The effects of APT content, initial pH value of the dye solution and temperature on adsorption were investigated. The adsorption kinetics and isotherms for MB dye onto the composites were studied, and the desorption properties of the composites were also discussed.

2. Materials and methods

2.1. Materials

Acrylic acid (AA, distilled under reduced pressure before use), ammonium persulfate (APS, recrystallized from distilled water before use) and *N,N'*-methylenebisacrylamide (MBA, used as received) were supplied by Shanghai Reagent Corp. (Shanghai, China). Chitosan (CTS, degree of deacetylation is 85%, average molecular weight is 9.0×10^5) was supplied by Zhejiang Yuhuan Ocean Biology Co. (Zhejiang, China). Attapulgit (APT, supplied by Linze Colloidal Co., Gansu, China) was milled through a 320 mesh screen and treated with 37% hydrochloric acid for 72 h, followed by washing with distilled water until pH=6.0 was achieved, and then dried at 105 °C for 8 h before use. The molecular formula of MB (Shanghai Reagent Corp., China) is $C_{16}H_{18}N_3S$ and the molecular structure is shown in Fig. 1. Other agents used were all of analytical grade and all solutions were prepared with distilled water.

2.2. Preparation and characterization of adsorbents

A series of CTS-g-PAA/APT composites from CTS, AA and APT was prepared according to our previous reports [34]. The preparation procedure of CTS-g-PAA was similar to that of CTS-g-PAA/APT except without APT. The products were milled and all samples used for testing had a particle size of 200 mesh.

IR spectra were recorded on a Thermo Nicolet NEXUS TM spectrophotometer using KBr pellets. The absorption band varieties of IR spectra of APT, CTS, CTS-g-PAA and CTS-g-PAA/APT show that graft reaction has taken place among CTS, AA and APT. The micrographs of samples were taken using SEM (JSM-5600LV, JEOL, Ltd.). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold. The results of morphological analysis indicate that CTS-g-PAA/APT has a relatively loose and fibrous surface compared with CTS-g-PAA [34].

2.3. Determination of pH_{PZC} of adsorbent

The point of zero charge (pH_{PZC}) of samples was determined by the solid addition method [35]. To a series of 100 mL conical flasks 45 mL of KNO_3 solution of known strength was transferred. The pH_0 values of the solution were roughly adjusted from 2 to 12 by adding either

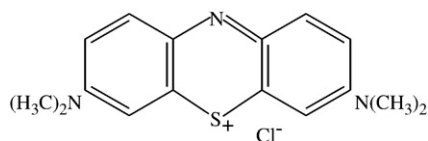


Fig. 1. Structure of MB.

0.1 mol/L HNO_3 or NaOH. The total volume of the solution in each flask was made exactly to 50 mL by adding the KNO_3 solution of the same strength. The pH of the solutions was then accurately noted, and 0.1 g of samples was added to each flask, which were securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the supernatant liquid were noted. The difference between the initial (pH_0) and final pH (pH_f) values ($pH_0 - pH_f$) was plotted against the pH. The point of intersection of the resulting curve at which pH gave the pH_{PZC} . The procedure was repeated for different concentrations of KNO_3 .

2.4. Adsorption studies

All batch experiments were performed on a thermostated shaker (THZ-98A) with a shaking of 120 rpm. The effects of the amount of APT on dye removal were carried out in the 50 mL of dye solutions (2000 mg/L, pH 5.0) with 0.05 g of adsorbent at 30 °C for 60 min. The influence of pH on MB removal was studied by adjusting MB solutions (2000 mg/L) to different pH values (2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0) using a pH meter (DELTA-320) and agitating 50 mL of dye solution with 0.05 g of adsorbent at 30 °C for 60 min. The effect of temperature on dye removal was carried out in the 50 mL of dye solutions (2000 mg/L, pH 5.0) with 0.05 g of adsorbent for 60 min.

For kinetic study, 2000 mg/L dye solutions (50 mL, pH 5.0) were agitated with 0.05 g of adsorbent at 30 °C for predetermined intervals of time. Batch equilibrium adsorption experiments were carried out by agitating 50 mL various concentrations of MB solutions at pH 5.0 with 0.05 g of adsorbent at 30 °C until equilibrium was established.

The samples were withdrawn from the shaker at predetermined time intervals and the dye solution was separated from the adsorbent by centrifugation at 4500 rpm for 10 min. The absorbencies of samples were measured using a UV-vis spectrophotometer (Specord 200) at wavelength 670 nm (MB has a maximum absorbency at wavelength 670 nm) on a UV-vis spectrophotometer. Then the concentrations of the samples were determined by using linear regression equation ($y = 0.1751x - 0.1145$, $R^2 = 0.9998$) obtained by plotting a calibration curve for dye over a range of concentrations. The amounts of MB adsorbed onto samples were calculated by subtracting the final solution concentration from the initial concentration of dye solutions.

2.5. Desorption studies

For batch desorption study, the adsorbent utilized for the adsorption of an initial dye concentration of 2000 mg/L was separated from the dye solution by centrifugation. The dye-loaded adsorbent was washed gently with water to remove any unadsorbed dye. Then the spent adsorbent was stirred using a magnetic stirrer with 50 mL of distilled water at different pHs for 60 min. The desorbed dye was determined as mentioned before.

3. Results and discussion

3.1. Effect of APT content on adsorption

The influence of APT content on the adsorption capacities of CTS-g-PAA/APT composites was shown in Fig. 2. As shown in Fig. 2, the adsorption capacity of CTS-g-PAA/APT composite was little higher than that of CTS-g-PAA when APT content was less than 20%. Compared with CTS-g-PAA (1868 mg/g), the adsorption capacities of CTS-g-PAA/APT composites with APT content of 2%, 5% and 10% are 1896, 1884 and 1870 mg/g, respectively. According to our previous study [36,37], -OH on the surface of APT could react with acrylic acid, which could improve the polymeric network, and then enhance the adsorption capacity to a certain extent. CTS-g-PAA shows a tight surface, however, the introduction of APT forms a relatively loose

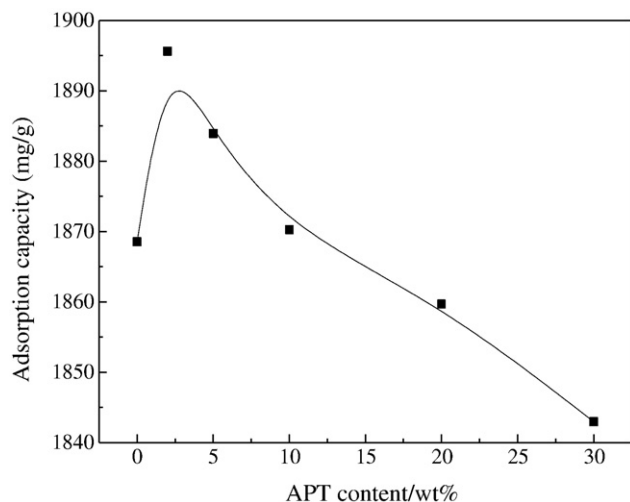


Fig. 2. Effect of APT content on the adsorption capacity of CTS-g-PAA/APT for MB. Adsorption experiments—dye concentration: 2000 mg/L; sample dose: 0.05 g/50.00 mL; pH: 5.0; temperature: 30 °C; equilibrium time: 60 min.

and fibrous surface [34]. This surface may be convenient for the penetration of dye molecules into the polymeric network of the composites, leading to the increase in the absorption capacity of MB to a certain extent. Nevertheless, further increasing APT content from 20% to 30% resulted in a decrease of absorption capacity. The decreasing tendency of adsorption capacity with increasing APT content may be attributed to the following facts. APT could react with AA and there are lots of -OH groups on the surface of APT, thus APT particles may act as crosslinking points in the network. Consequently, higher APT content results in the generation of more crosslink points and the decrease of elasticity of the polymer chains, which decreases the adsorption capacity of the composites. Additionally, the content of hydrophilic groups is lower at a higher APT content, which also caused the shrinkage of the composites and then decreased the adsorption capacity. However, the adsorption capacity of the composites with APT content of 30% (1843 mg/g) decreased lesser than that of the composite with APT content of 2% (1896 mg/g). Moreover, the cost of APT is much lower than those of AA and CTS. Therefore, considering the economic advantage, the following discussion will be focused on the CTS-g-PAA/APT composites with APT content of 30%.

3.2. Effect of pH value on adsorption

To understand the adsorption mechanism, it is necessary to determine the point of zero charge (pH_{PZC}) of the adsorbent [38]. Adsorption of cations is favored at $pH > pH_{PZC}$, while the adsorption of anions is favored at $pH < pH_{PZC}$. The specific adsorption of cations shifts pH_{PZC} towards lower values, whereas the specific adsorption of anions shifts pH_{PZC} towards higher values. The experimental results show that the pH_{PZC} values of CTS-g-PAA and CTS-g-PAA/APT are 5.0 and 5.1, respectively.

The pH value of the dye solution is an important factor for the determination of the adsorption of solutes [39]. Fig. 3 shows the effect of pH value of dye solution on the adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT. It was found that with the pH value increased from 2.0 to 5.0, the adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT sharply increased from 1113 to 1868 mg/g and from 1085 to 1843 mg/g, respectively, and then increased continuously from 1868 to 1939 mg/g and from 1843 to 1900 mg/g with further increase in pH from 5.0 to 9.0. This phenomenon may be interpreted as follows: on one hand, most of the carboxylic groups in CTS-g-PAA and CTS-g-PAA/APT are ionized and interacted with the dye molecules via the strong

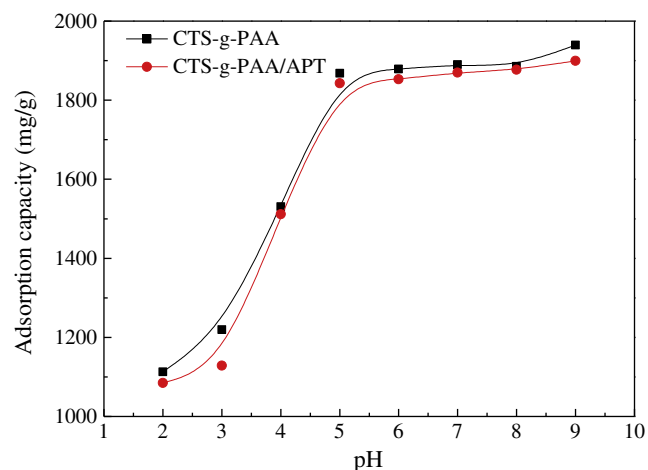


Fig. 3. Effect of the pH values on the adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT for MB. Adsorption experiments—dye concentration: 2000 mg/L; sample dose: 0.05 g/50 mL; temperature: 30 °C; equilibrium time: 60 min (APT content in the feed is 30%).

electrostatic interaction, which is favorable to increase the absorption for MB. On the other hand, the -COOH groups present in acrylate dissociate to form COO^- at higher pH, which increases the number of fixed ionized groups and generates the electrostatic repulsion forces among the adjacent ionized groups. This induces an expansion of the polymer network and results in an increase of the absorption for MB. However, comparatively high adsorption capacities of cationic dye on the adsorbents still occurred at pH 2.0 due to the occurrence of chemical interactions between MB dye and adsorbents. This can be further proved by the desorption studies. Similar trend can also be observed in the adsorption of MB on the hydrogel formed by modified gum arabic, polyacrylate and polyacrylamide [33] and CTS-g-PAA/MMT [34].

Fig. 4 shows variation of pH with time for the adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT. As can be seen from Fig. 4, the system pH changes swiftly during the initial 15 min and, thereafter, the change is gradual. After about 30 min, pH remains almost invariant with time. Maximum pH change is found for CTS-g-PAA and CTS-g-

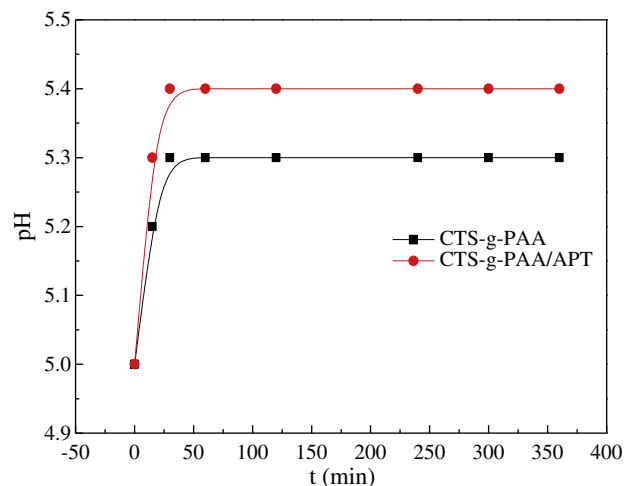


Fig. 4. Variation of pH with time for adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT for MB. Adsorption experiments—dye concentration: 2000 mg/L; sample dose: 0.05 g/50 mL; pH: 5.0; temperature: 30 °C; equilibrium time: 60 min (APT content in the feed is 30%).

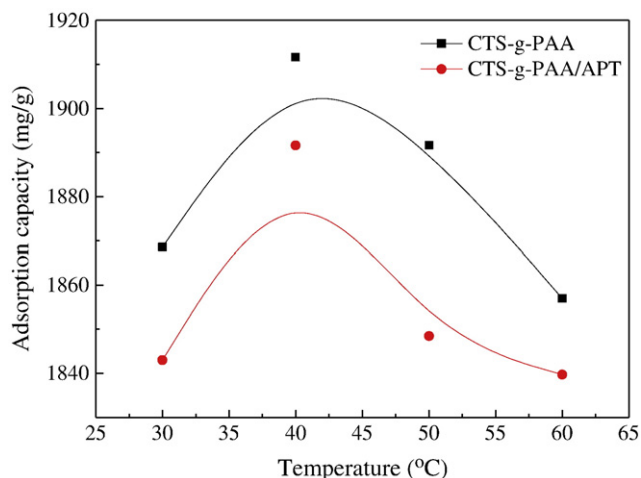


Fig. 5. Effect of the temperature on the adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT for MB. Adsorption experiments—dye concentration: 2000 mg/L; sample dose: 0.05 g/50 mL; pH: 5.0; equilibrium time: 60 min (APT content in the feed is 30%).

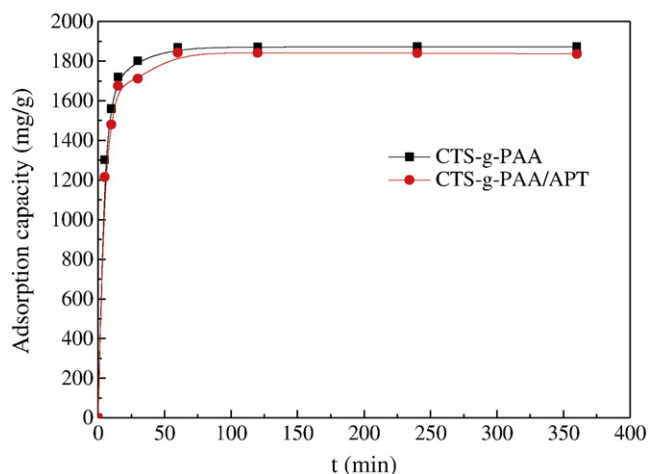


Fig. 6. Effect of the adsorption time on adsorption capacity of CTS-g-PAA/APT for MB. Adsorption experiments—dye concentration: 2000 mg/L; sample dose: 0.05 g/50 mL; pH: 5.0; temperature: 30 °C (APT content in the feed is 30%).

PAA/APT: pH increase from 5.0 to about 5.3 and from 5.0 to about 5.4, respectively. The extent of pH change during sorption process may not affect the sorption equilibrium and kinetics significantly [40]. Therefore, further study on adsorptive removal of dyes by CTS-g-PAA and CTS-g-PAA/APT was carried out at pH 5.0.

3.3. Effect of temperature on adsorption

It is important to investigate the effect of temperature on adsorption in a view of practical application. Fig. 5 shows the relationship between the temperature and the adsorption capacities of MB by CTS-g-PAA and CTS-g-PAA/APT, respectively. With increasing temperature from 30 °C to 40 °C, the adsorption capacities increased from 1868

to 1912 mg/g, and from 1843 to 1892 mg/g for CTS-g-PAA and CTS-g-PAA/APT, respectively. However, with further increasing temperature from 40 °C to 60 °C, the adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT decreased from 1912 to 1857 mg/g, 1892 to 1840 mg/g, respectively. It is well known that increasing temperature may produce a swelling effect within the internal structure of absorbent, penetrating the large dye molecule further [41]. However, the mobility of the large dye ions increases with increasing temperature, which leads to a decrease in the adsorption capacity of composite with further increasing temperature. The same phenomenon was also observed by our previous study [42].

3.4. Adsorption kinetics

Fig. 6 shows the effect of the adsorption time on the adsorption capacities of MB by CTS-g-PAA and CTS-g-PAA/APT, respectively. It is clear that the adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT increased rapidly with the increase of the adsorption time from 0 to 15 min and more than 90% of the equilibrium adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT all occurred within 15 min. It can be seen from Fig. 6 that the adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT gradually increased with the increase of the adsorption time from 15 to 60 min until equilibrium. Therefore, under our experimental conditions, the equilibrium times for the adsorption of MB on CTS-g-PAA and CTS-g-PAA/APT are all 60 min.

To investigate the potential rate-controlling steps involved in the adsorption of MB onto CTS-g-PAA and CTS-g-PAA/APT, both pseudo-first-order and pseudo-second-order kinetic models were used to fit the experimental data.

The pseudo-first-order rate expression of Lagergren model [43] is generally expressed as follows:

$$\frac{dq_e}{dt} = k_1(q_e - q_t). \quad (1)$$

After integration with the initial condition $q_t = 0$ at $t = 0$, Eq. (2) can be obtained:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}. \quad (2)$$

The pseudo-second-order rate equation is given as [44]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_e and q_t are the amounts of adsorption dye (mg/g) at equilibrium and at time t (min), k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the adsorption rate constant of pseudo-first-order and pseudo-second-order adsorption rates, respectively. The linear plots of $\log(q_e - q_t)$ versus t and (t/q_t) versus t are drawn for the pseudo-first-order and the pseudo-second-order models, respectively. The rate constants k_1 and k_2 can be obtained from the plot of experimental data.

The rate constants, the correlation coefficients and the calculated q_e for the two kinetic models of CTS-g-PAA and CTS-g-PAA/APT are shown in Table 1. As seen from Table 1, the correlation coefficients (R^2) of the pseudo-first-order model were 0.8091 and 0.7406 for CTS-

Table 1
The rate constants, the correlation coefficients and the calculated q_e of the two kinetic models.

Samples	Pseudo-first-order model			Pseudo-second-order model		
	k_1 ($\times 10^{-2} \text{ min}^{-1}$)	R^2	q_e	k_2 ($\times 10^{-4} \text{ g/mg/min}$)	R^2	q_e
CTS-g-PAA	1.55	0.8091	125	4.52	0.9999	1882
CTS-g-PAA/APT	1.35	0.7406	170	3.90	0.9999	1847

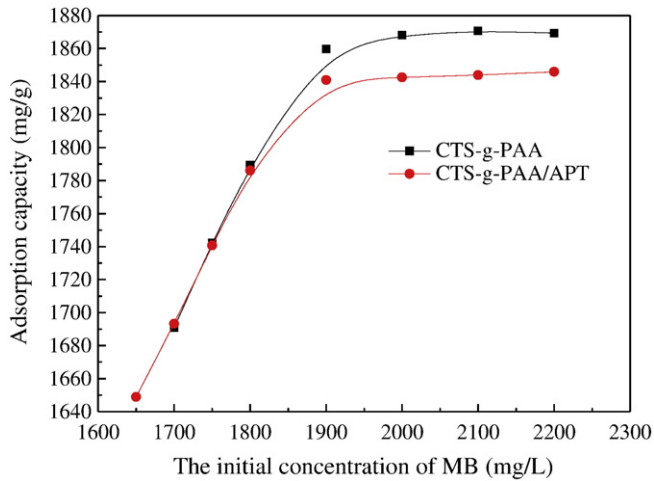


Fig. 7. Effect of the initial dye concentration on the adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT for MB. Adsorption experiments—sample dose: 0.05 g/50 mL; pH: 5.0; temperature: 30 °C; equilibrium time: 60 min (APT content in the feed is 30%).

g-PAA and CTS-g-PAA/APT, respectively. For the pseudo-second-order model, the correlation coefficients (R^2) of the pseudo-second-order model were all 0.9999 for CTS-g-PAA and CTS-g-PAA/APT. In addition, the calculated q_e values of the pseudo-first-order model for the adsorption of MB by CTS-g-PAA and CTS-g-PAA/APT were 125 and 170 mg/g, respectively. For the pseudo-second-order model, the calculated q_e values of CTS-g-PAA and CTS-g-PAA/APT were 1882 and 1847 mg/g, respectively. Obviously, the calculated q_e values of CTS-g-PAA and CTS-g-PAA/APT agreed with the experimental data (1869 and 1843 mg/g) in the case of the pseudo-second-order model. These results indicated that the adsorption of MB on CTS-g-PAA and CTS-g-PAA/APT followed the pseudo-second-order rather than the pseudo-first-order.

3.5. Adsorption isotherms

The influence of the initial dye concentration on adsorption capacities of MB for CTS-g-PAA and CTS-g-PAA/APT is shown in Fig. 7. It is clear that the initial dye concentration plays an important role in the adsorption capacity. The results show that the adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT increased sharply from 1691 to 1860 mg/g and from 1649 to 1841 mg/g when the initial concentration of dye increased from 1700 to 1900 mg/L and from 1650 to 1900 mg/L, respectively. However, the adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT hardly increased with further increase in the initial dye concentration.

Adsorption isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface. Hence, the correlation of equilibrium data using either a theoretical or empirical equation is essential for the adsorption interpretation and prediction of the extent of adsorption [45]. The equilibrium adsorption data were generally interpreted using Langmuir and Freundlich models [46] which are represented by the following equations, respectively:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (4)$$

$$q_e = K_f C_e^{1/n} \quad (5)$$

where q_m (mg/g) and b (L/mg) are Langmuir isotherm coefficients. The value of q_m represents the maximum adsorption capacity. K_f (mg/g) and n are Freundlich constants. Two adsorption isotherms were constructed by plotting the C_e/q_e versus C_e , $\log q$ versus $\log C_e$, respectively.

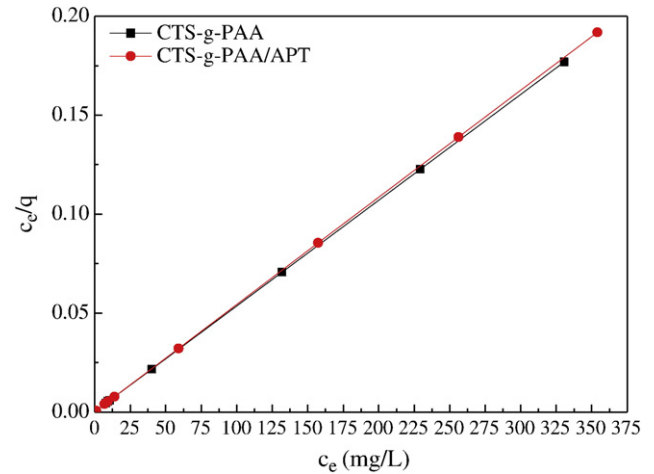


Fig. 8. Langmuir plot for the adsorption of MB by CTS-g-PAA and CTS-g-PAA/APT.

Fig. 8 shows the linear plot of C_e/q_e versus C_e for the Langmuir models of adsorption of MB onto CTS-g-PAA and CTS-g-PAA/APT, respectively. The applicability of the Langmuir isotherm suggests the monolayer coverage of the dye on the surface of CTS-g-PAA and CTS-g-PAA/APT. Similar behavior was also found for the adsorption of MB onto precursor and quaternary ammonium compounds modified montmorillonite [16], Cu(II)-exchanged montmorillonite [47], clay [24] and CTS-g-PAA/MMT [42]. The values of R^2 for CTS-g-PAA and CTS-g-PAA/APT are all 1. The q_m values for the adsorption of MB by CTS-g-PAA and CTS-g-PAA/APT were 1873 and 1848 mg/g, respectively, which were the same as those found by experimental data 1868 and 1843 mg/g for CTS-g-PAA and CTS-g-PAA/APT, respectively. The q_m values of MB on CTS-g-PAA and CTS-g-PAA/APT have been compared with those of other adsorbents (Table 2). It can be seen that the q_m value of CTS-g-PAA/APT was much higher than those of other adsorbents such as MMT, clay, and SH. Moreover, the q_m value of CTS-g-PAA/APT was less than those of CTS-g-PAA and CTS-g-PAA/MMT composites. Thus, CTS-g-PAA/APT composites can be effectively used as an adsorbent in treatment of wastewaters containing MB dye. Fig. 9 shows that the values of R^2 of Freundlich model for CTS-g-PAA and CTS-g-PAA/APT are 0.9158 and 0.9446, respectively. So, the adsorption of CTS-g-PAA and CTS-g-PAA/APT does not follow the Freundlich isotherm.

3.6. Desorption of MB

Desorption studies can help elucidating the mechanism of an adsorption process. If the dye adsorbed onto the adsorbent can be desorbed by water, it can be concluded that the attachment of the dye onto the adsorbent is by weak bonds. If the strong acids, such as HCl can desorb the dye, it can be concluded that the attachment of the dye onto the adsorbent is by ion exchange or electrostatic attraction [38]. Hence, distilled water of different pHs was used in the elution of dyes

Table 2

The q_m values for the adsorption of MB on different adsorbents.

Adsorbents	q_m (mg/g)	Ref.
CTS-g-PAA	1873	Our data in the paper
CTS-g-PAA/APT	1848	Our data in the paper
CTS-g-PAA/MMT	1859	[42]
MMT	322.6	[48]
Clay	58.2	[25]
SH	48	[33]

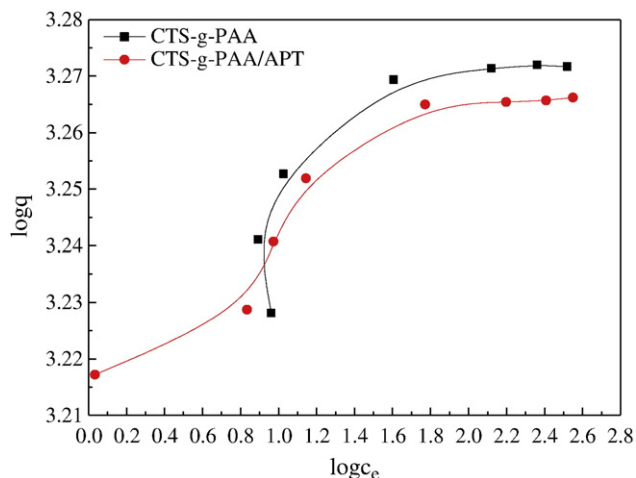


Fig. 9. Freundlich plot for the adsorption of MB by CTS-g-PAA and CTS-g-PAA/APT.

from CTS-g-PAA and CTS-g-PAA/APT. Fig. 10 shows the effect of pH on desorption percentage of dye from dye-loaded CTS-g-PAA and CTS-g-PAA/APT. It is obvious that the desorption percentage of CTS-g-PAA and CTS-g-PAA/APT decreased sharply with the increase of the pH of distilled water. Low desorption was obtained at pH 9.0 and the percentages of desorption for CTS-g-PAA and CTS-g-PAA/APT are only 1.1% and 2.3%, respectively. While in the case of pH 2.0, desorption percentages of 49.8% and 51.2% were obtained. The relatively high desorption amount at pH 2.0 suggests that adsorption of MB onto CTS-g-PAA and CTS-g-PAA/APT was carried out partially via electrostatic attraction, which further substantiated the discussion about the effect of pH value on adsorption. These results indicated that CTS-g-PAA and CTS-g-PAA/APT provided the potential for regeneration and reuse after adsorbed MB dye. In addition, the spent CTS-g-PAA and CTS-g-PAA/APT can be used as craftwork rockcrystal. Also, the spent CTS-g-PAA and CTS-g-PAA/APT also can be used as a fuel due to their high polymer content and the bottom ash after their combustion/incineration can be blended with clay/cement–concrete mixture to make bricks and building blocks for their safe disposal [42]. So, CTS-g-PAA and CTS-g-PAA/APT can be used as alternative-adsorbing agents in dye wastewater.

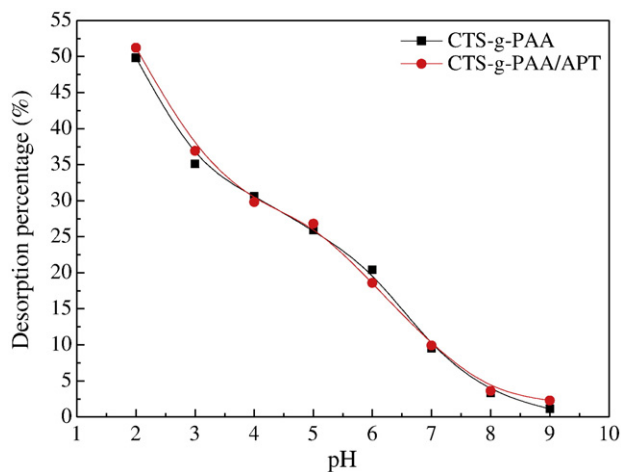


Fig. 10. Effect of pH on desorption percentage of dye from dye-loaded CTS-g-PAA and CTS-g-PAA/APT. Adsorption experiments—dye concentration: 2000 mg/L; sample dose: 0.05 g/50 mL; pH: 5.0; temperature: 30 °C; equilibrium time: 60 min (APT content in the feed is 30%).

4. Conclusion

Adsorption tests of MB dye on the CTS-g-PAA/APT composites were carried out and the obtained results showed that MB adsorption process is dependent on APT content, initial pH value of the dye solution and adsorption temperature. APT content has certain influence on adsorption capacities of the composites. Introducing a small amount of APT could improve adsorption ability of the CTS-g-PAA composite to a certain extent. The adsorption capacities of CTS-g-PAA and CTS-g-PAA/APT for MB increased with increasing pH, but decreased with increasing temperature. The adsorption processes of the MB dye on CTS-g-PAA and CTS-g-PAA/APT followed the pseudo-second-order and the Langmuir isotherm, respectively. The Langmuir adsorption capacities were 1873 and 1848 mg/g for CTS-g-PAA and CTS-g-PAA/APT, respectively. In desorption studies, comparatively high desorption of dyes was obtained with pH 2.0 of distilled water. This indicates that CTS-g-PAA and CTS-g-PAA/APT provided the potential for regeneration and reuse after MB dye adsorption. Therefore, CTS-g-PAA and CTS-g-PAA/APT can be used as effective adsorbents for the removal of MB from wastewaters.

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