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Removal of methylene blue by Polyaniline/TiO₂ hydrate: Adsorption kinetic, isotherm and mechanism studies



^a Department of Environmental and Chemical Engineering, Xi'an Polytechnic University, Xi'an 710048, PR China

^b Department of Environmental Science and Engineering, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an 710049, PR China

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ABSTRACT

Polyaniline/TiO₂ (PANI/TiO₂), as a promising adsorbent, was synthesized and applied in the adsorption of methylene blue (MB) to evaluate the adsorption performance of PANI/TiO₂ for cationic dye. The effects of dosage, pH, temperature and ionic strength on the adsorption efficiency were investigated in details. The adsorption isotherm and kinetic studies were conducted and the results revealed that the adsorption of MB on PANI/TiO₂ was mainly controlled by chemical adsorption, membrane diffusion and intraparticle diffusion. The maximum adsorption capacity was 458.10 mg/g. HCl solution (0.1 mol/L) was used as stripping agent to study the regeneration stability of PANI/TiO₂, and the adsorption efficiency can be maintained over 99% after 10 cycles. The N_2 adsorption-desorption and Fourier Transform Infrared Spectroscopy of PANI/TiO₂ before and after adsorption were compared and analyzed to obtain the information of adsorption mechanisms. The adsorption of MB by TiO₂ mainly occurred on the surface hydroxyl and carboxyl groups, and was mainly heterogeneous multilayer physisorption. However, the adsorption of MB on PANI part occurred mainly on amino groups by hydrogen bonding and electrostatic interaction, and on benzene ring by π - π stacking and hydrophobic interaction, and was assigned to heterogeneous multilayer chemical adsorption by comparing the theoretical monolayer adsorption capacity and the actual adsorption capacity. After composition, PANI and TiO₂ cooperated in the adsorption process of MB and exhibited their respective advantages. The PANI/TiO₂ was an excellent adsorbent for organic cation dyes and was expected to be a kind of universal adsorbent for multiple pollutants.

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1. Introduction

Nowadays, various kinds of organic dyes are developed and used in leather, electroplating, textile, paper-making, plastics and printing industries [1]. It was reported that 7×10^8 kg of dyestuffs were produced every year all over the world [2]. The complex aromatic structure of dyes make them stable and more difficult to be removed from the effluents [3]. However, the effluents containing dyestuffs without properly treatment can cause severe environmental problems [4]. Methylene blue (MB) is commonly used cationic dye for coloring cotton, wood, and silk. This dye has been studied because of its known strong adsorption affinity onto solid [5]. However, MB can cause a series of harms to humans and animals, such as eye burns, methemoglobinemia, dyspnea, irritation to the skin [6]. Thus, the MB, as a typical cationic dye, has often been chosen as a model compound to investigate the adsorption process from aqueous solutions [7].

Chemical, biological and physical treatment processes aiming at removing pollutants from wastewater have been developed and widely applied [8]. Among these techniques, adsorption has been widely

* Corresponding authors. E-mail addresses: fjtes@mail.xjtu.edu.cn (J. Feng), yanwei@xjtu.edu.cn (W. Yan). researched and applied due to its low-cost and high-efficient features, as well as operational ease [9,10]. It demonstrates superior removal efficiency to other techniques, especially for refractory wastewater and low concentration wastewater. Currently, the adsorbents including activated carbon [11], resin and gel [12], graphene [13], metal oxide [14], and polymer [15–17] had been well investigated. They all possess their own unique advantages, and limitations as well. There is a lack of widely applicable adsorbents for simultaneous adsorption of various pollutants in complex printing and dye wastewater.

An excellent adsorbent should possess large specific surface area, suitable porous structure, ease of preparation and regeneration, high adsorption capacity and robustness [18,19]. Organic and inorganic composite material as adsorbent can improve the synergistic adsorption and expand the application [20,21]. In our previous studies, the PANI/TiO₂ composite had been synthesized and demonstrated as an adsorbent for anion-type pollutants such as phosphate ions [22] and anionic azo dyes (Acid red G, ARG) [23]. The adsorption performance of TiO₂ was due to the porous structure and the hydroxyl groups on the surface. However, the regeneration efficiency was very low and the cost for regeneration was high. The conductive polyaniline (PANI) possesses rigid organic skeleton and reversible doping-dedoping property, and the morphology is easily modulated [24], which benefit the adsorption







and regeneration. PANI and TiO_2 had been individually studied as adsorbent for different pollutants such as Cr(VI) [25], Pb(II) [26], methyl orange [27], Reactive Red 195 [28], phosphate ions [29]. And outstanding adsorption capacity and high stability of PANI/TiO₂ for phosphate ions and anionic dyes were observed in our previous studies. It is necessary to further study the adsorption behavior and mechanism of this adsorbent for other typical pollutants.

In this paper, the adsorption behavior and mechanism of PANI/TiO₂ for MB cations were detailed to further study the wide applicability of PANI/TiO₂. The influence factors on adsorption, like pH, temperature, ionic strength, and initial MB concentration were investigated. The potential adsorption mechanisms were finally analyzed and proposed with the aid of N₂ adsorption-desorption and FT-IR characterizations before and after adsorption. In order to have a more accurate and indepth understanding of the adsorption mechanism of the composite adsorbent, the control studies of PANI and TiO₂ were made for all the above items. These studies can not only expand PANI/TiO₂ applications but also be helpful to understand the adsorption mechanism of PANI/TiO₂ for MB.

2. Materials and methods

2.1. Materials

Methylene blue (MB, $C_{16}H_{18}N_3$ ClS, Mw 319.85) was purchased from Beijing Chemical Reagents Company, and other reagents were from Sinopharm Chemical Reagent Co., Ltd. Aniline (99.5%) was distilled under reduced pressure, and stored in darkness at 0 °C under N₂ atmosphere prior to use. All other chemicals were used as received.

2.2. Preparation of PANI/TiO₂

PANI/TiO₂ was synthesized using a one-pot chemical oxidative polymerization method. TiO₂ nanoparticles were hydrolyzed from titanium isopropoxide in 100 mL mixture solution of HNO₃ (0.064 mol/L) and citric acid (0.1 mol/L) in a three-necked flask. After magnetic stirring for 1.0 h, aniline (1.8 mL) monomer was added to the suspension liquid and stirred for 1 h. Then, ammonium persulphate (APS) solid was added to the mixture slowly under mechanical stirring and the polymerization reaction lasted for another 8 h at ambient temperature. The collected precipitates were rinsed with distilled water and ethanol, and then dried at 60 °C for 48 h. PANI and TiO₂ were also prepared under the same condition as controls.

2.3. Adsorbents characterization

The morphology was characterized by scanning electron microscopy (SEM) (JSM-6700F, JEOL). Physical properties of the samples before and after the adsorption test was carried out by the Builder SSA-4200 at 77 K using the Barrett-Joyner-Halenda (BJH) method. The surface functional groups of samples were analyzed by FTIR using the KBr pellet method on a BRUKER TENSOR 37 FT-IR spectrophotometer. The Zeta potentials of adsorbents at different pH were measured with Malvern Zetasizer Nano ZS90. A stock solution of MB (1000 mg/L) was prepared by dissolving MB in distilled water, which was diluted for use as working solutions with a pre-designed concentration. The concentration of MB was determined by the UV–Vis spectrophotometer at $\lambda_{max} = 664$ nm (Agilent 8453).

2.4. Adsorption

Batch adsorption experiments were conducted by mixing the adsorbent with the MB solution in a conical flask, and the flask was settled on a constant temperature oscillator at 220 rpm. The suspension was centrifuged at 4000 rpm for 5 min, and the MB concentration in the supernatant was determined. The influence of the pH on the adsorption was investigated by employing the adsorbents to treat MB solutions at different pH (pH = 1.0-11.0). The NaOH (0.1 mol/L) and HCl (0.1 mol/L) solutions were used to adjust the pH. Due to the complexity of real effluent, the effect of ionic strength on the adsorption was studied during the adsorption process with the coexistence of NaCl at different concentrations (5–1500 mmol/L).

The adsorption isotherm experiment was conducted with different initial MB concentration (5–2000 mg/L) to determine the maximum adsorption capacity and the suitable isotherm model of the adsorbents for MB. Three levels of tempertures (298 K, 308 K and 318 K) were chosen to study the effect of temperature on adsorption.

The adsorption equilibrium of MB (400 mg/L) onto PANI/TiO₂ was evaluated at 298 K, 308 K and 318 K, with the optimal dosage of PANI/TiO₂ in 10 h. 10 mL of the mixture was fetched in the regular interval and filtrated with a 0.45 μ m Syringe-driven Filter for monitoring the MB concentration.

The adsorption rate R (%) and the amount of adsorbed dye on per gram of adsorbent (Q_t (mg/g)) in time *t* were calculated by the Eqs. (S1) and (S2) in Supplementary material.

2.5. Regeneration

Due to the reversible doping/dedoping chemistry of PANI, the as-prepared composites can be regenerated by simple acid and alkali treatment theoretically. Therefore, 0.1 mol/L HCl and 0.1 mol/L NaOH solutions were used to treat the used adsorbents for 10 min sequentially. Then the regenerated adsorbent was reused for the adsorption experiments. The adsorption rate and adsorption capacity of regenerated adsorbents were calculated by Eqs. (S3)–(S6) in Appendix S1. Both adsorption and desorption processes were equilibrated for 12 h at 298 K in an oscillator with 220 rpm.

3. Results and discussion

3.1. PANI, TiO₂ and PANI/TiO₂ characterization

The samples PANI, TiO₂ and PANI/TiO₂ were characterized by SEM, N₂ adsorption-desorption and FTIR, and the results are displayed in Fig. 1 and Figs. S1, S2. The TiO₂ particles were uniform in a diameter of <1 μ m (Fig. 1a), but the PANI was laminated structure (Fig. 1b) from the SEM patterns. After composition, the particles were more rough than that of TiO₂, making the particles appeared to have a layered surface structure (Fig. 1c). This was speculated to the result of the deposition of PANI sheets [30]. The EDS confirmed this speculation (Fig. S1), and the Ti element was also detected, implying that the TiO₂ was not covered completely by PANI sheets. And according to the FTIR of PANI and PANI/TiO₂, it confirmed the present of PANI in the composite [23]. The PANI/TiO₂ was actually a core-shell structure with PANI partially covering the TiO₂. The schematic diagram of PANI/TiO₂ composition mechanism is exhibited in Fig. 1d.

The TiO₂ was actually titanium dioxide hydrate with rich hydroxyl and carboxyl groups on the surface as revealed by FTIR (Fig. S2) [31]. After dosed into the acid solution, the TiO₂ particles was negatively charged on the surface. Meanwhile, the aniline monomers in acid solution ionized and were positively charged, which were attracted to the surface of TiO₂ hydrates. The polymerization reaction was triggered by APS. And the interaction, like hydrogen bond, electrostatic attraction and coordination interaction, combined the PANI and TiO₂ together into PANI/TiO₂.

The settlement performance of samples were compared in Fig. S4. It can be found that after composition of PANI and TiO₂, the settlement property was improved obviously, which facilitated sample recovery from solution.



Fig. 1. The morphology of TiO₂(a), PANI(b) and PANI/TiO₂(c) and the schematic diagram of PANI/TiO₂ compound mechanism(d).

3.2. Adsorption

The optimal dosage of adsorbent was 2 g/L in adsorption process (Fig. S3). The effect of pH on adsorption was studied over a range of 1–11. In the pH range of 1–11, the characteristic peaks of MB in the UV–Vis spectrum remained unchanged before and after adsorption (Fig. S5). From Fig. 3a, the adsorption efficiency was higher than 95% over the pH range of 3–11 by PANI, TiO₂ and PANI/TiO₂, respectively. However, the adsorption efficiency plunged when the pH was lower than 3 in a descending order: PANI/TiO₂ > PANI > TiO₂. PANI/TiO₂ showed stronger pH buffer capacity than that of PANI and TiO₂. It is also noticed that the higher the concentration of MB, the harder the adsorption of MB may happen.



Fig. 2. The ZETA potential of TiO₂, PANI and PANI/TiO₂(5 mg dissolved into 10^{-3} mol/L NaCl solution; HCl and NaOH for pH adjustment).

According to the Zeta potentials (in Fig. 2) at different pH, the isoelectric point (pH_{iep}) of PANI, TiO₂ and PANI/TiO₂ were 7.05, 2.66 and 5.21, respectively. Combining with Zeta potential and the influence of pH on adsorption (Fig. 3a), PANI showed high removal efficiency for MB by electrostatic attraction over the pH range of 7.05–11; the adsorption efficiency decreased obviously in the range of 1–3 due to the electrostatic repulsion [32]. However, when the pH was in the range of 3.00–7.05, the adsorption efficiency of PANI for MB was still high. The same phenomenon occurred in the adsorption of MB onto PANI/TiO₂ in the pH range of 3.00–5.21 as well. It was thought that there were other interactions involved in the adsorption process of PANI and PANI/TiO₂ for MB, besides electrostatic attraction.

The effect of ionic strength on the adsorption was recorded in Fig. 3b. As the concentration of NaCl increased, the removal efficiency of PANI dropped gradually. The effects on the adsorption by TiO₂ was relatively complex: dropped significantly followed by a sharp increase. The UV-Vis spectrum of MB solution showed no change during the adsorption (Fig. S6a), suggesting the stability of MB chromophoric group and no degradation and photolysis happened in the process. The experimental phenomena were recorded in Fig. S6b after adsorption of MB by TiO₂. It can be seen that TiO₂ was uniformly blue after adsorption at 60 mmol/L of NaCl. However, TiO₂ kept the original white after adsorption of MB at 1000 and 1500 mmol/L of NaCl. The MB blue precipitate layer formed upon the TiO₂ sample. The salting-out effect occurred during the adsorption of MB by TiO₂ [33]. In Fig. 3b, green dash line showed the salting-out effect of 200 mg/L MB solutions with different dosages of NaCl. The salting-out of MB occurred when the NaCl concentration was higher than 300 mmol/L. The salting-out is unfavorable to adsorption. In contrast, the effect of ionic strength on the adsorption of PANI/ TiO₂ was moderate.

The adsorption efficiencies of PANI/TiO₂, PANI and TiO₂ for MB solution with different initial concentrations were determined at three temperatures (298 K, 308 K and 318 K). Rising temperature was favor for the adsorption efficiency of MB onto PANI/TiO₂, PANI and TiO₂ (Fig. 3c). This indicated that chemical reaction was involved in the



Fig. 3. The MB removal rate of adsorbents at different pH (a), with different concentrations of NaCl coexisting (the dash green curve was the salting-out ratio of MB (200 mg/L) (b), the effect of initial MB concentration (5–2000 mg/L at pH 9) on adsorption efficiency (c) and adsorption capacity (d) (All adsorptions here were conducted at 298 K for 12 h). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

adsorption process. Adsorption efficiency of TiO_2 for MB was always above 90% regardless of MB concentration. However, the adsorption efficiencies of PANI and PANI/TiO₂ decreased gradually with the increased initial concentration of MB. From Fig. 3d, it can be found that the adsorption capacity of PANI/TiO₂, PANI and TiO₂ increased with the increase of MB initial concentration.

The adsorption equilibrium of MB (400 mg/L) on PANI/TiO₂ at three temperatures are displayed in Fig. S7. The PANI/TiO₂ showed the same final adsorption capacity after 10 h, but a longer adsorption equilibrium time was required at a higher temperature. The reason can be explained that as the temperature increased, the molecular motion and collision intensified, increasing the probability of adsorption. However, the molecular interaction force was weakened, which reduced the adsorption rate and extended the adsorption equilibrium time. But in the end, the final adsorption amount remains unchanged. The equilibrium adsorption of PANI/TiO₂ for MB can be achieved within 120 min at 298 K.

Above all, adsorption performance of PANI/TiO₂ for MB was more excellent than that of PANI and TiO₂ from the effects of pH and ionic strength point. Although the TiO₂ and PANI showed higher adsorption efficiencies than PANI/TiO₂, the evaluation of an adsorbent based more than on the adsorption efficiency.

3.3. Desorption and regeneration

Desorption efficiency is an important index for evaluating adsorbent for practical applications.

The adsorption efficiency of MB by different samples with different pretreatments are listed in Table S1. It can be observed that the adsorbents treated by NaOH solution exhibited excellent efficiency for 300 mg/L MB solution. The adsorption efficiencies of PANI and TiO₂ for MB can both reach over 98%. PANI/TiO₂ treated by NaOH solution can adsorb 99.76% of MB. While the adsorption efficiency of MB on PANI/TiO₂ treated by HCl or no treatment was lower than 15%, which can be concluded that electrostatic attraction made great contribution to the adsorption, which was in accord with the results of pH effects. Based on the influence of pH on adsorption, the exhausted adsorbents were treated by 0.1 mol/L HCl to release MB from the adsorbents. The regeneration experiment was conducted both in light and in dark, and the desorption and readsorption efficiency are displayed in Fig. 4.

As can be seen, illumination had no effect on the removal efficiency of MB by three adsorbents, eliminating the possibilities of photocatalytic degradation of MB. In Fig. 4a, the desorption efficiency of MB from TiO₂ declined gradually, which may be due to the dissolution of TiO₂ hydrate in the HCl solution during the treatment process. For PANI, the adsorption efficiency of MB remained above 80% (Fig. 4b). The composite PANI/TiO₂ exhibited high adsorption efficiency for MB, and the desorption efficiency was relatively stable in five cycles (Fig. 4c). The phenomenon of unequal adsorption and desorption of these three adsorbents may be ascribed to the unsaturated adsorption sites for MB in every adsorption cycle. Above all, while the adsorption capacities of TiO₂ and PANI for MB were higher than that of PANI/TiO₂, the composite PANI/



Fig. 4. The regeneration efficiency of the TiO₂(a), PANI(b) and PANI/TiO₂(c) by HCl solution. Experiment condition: (300 mg/L MB, adsorption for 12 h, desorption for 12 h, 298 K).

 TiO_2 had higher stability in regeneration application. The adsorption efficiency of PANI/TiO_2 for 100 mg/L MB can be maintained over 99% after 10 cycles (Fig. S8).

In order to eliminate the redox conversion from blue oxidation state to colorless reduction state of MB molecular (Fig. S9) [34,35], the removal rate of MB concentration (initial concentration: 200 mg/L), chemical oxygen demand (COD) and total organic carbon (TOC) after adsorption by TiO₂, PANI and PANI/TiO₂ were determined, the results are shown in Fig. S10. From Fig. S10, the removal rate of MB concentration were in accord with that of TOC and COD, showing that the molecular structure transformation of MB did not occur in adsorption process. Combined with the illumination and dark absorption experiments, the removal of MB mainly resulted from adsorption [36–43].

Compared with other MB dye adsorbents reported (listed in Table 1), it can be found that $PANI/TiO_2$ possessed out-standing adsorption properties for MB, such as high adsorption capacity, wide pH applicability, and good performance of regeneration. These superior performances indicated that $PANI/TiO_2$ is potential adsorbent for cationic dyes. Therefore, further study on the adsorption mechanisms of $PANI/TiO_2$ for cationic dye MB is significant and valuable.

3.4. Adsorption kinetics

In order to study the control mechanisms, the adsorption process of TiO₂, PANI and PANI/TiO₂ for 533 mg/L MB were monitored at 298 K, and the results were fitted by kinetics models, including pseudo-first-order [44], pseudo-second-order [45,46], and Elovich [47]. The mathematical expressions and descriptions of the three models are listed in SI (Eq. S7-S9) in Appendix S2). The experimental data and fitting plots are exhibited in Fig. S11.

The adsorption of MB onto TiO_2 was within 5 min to achieve the adsorption equilibrium; but a much longer time of 240 min and 120 min were required to reach the adsorption equilibrium of PANI and PANI/ TiO_2 , respectively (Fig. S11). The fitting parameters of these models

Table 1					
Adsorption	performances	for MB	onto	various	adsorbents

Adsorbents	Dyes	pН	$Q_m(mg/g)$	t (min)	Sources
PANI/TiO ₂	MB	3–10	458.10	120	This study
PANI-NT/SiO ₂	MB	-	10.31	10	[36]
PANI hydrogel	MB	>6.5	71.20	180	[37]
PDA	MB	7-10	90.7	60	[38]
A pH-responsive resin	MB	3–7	-	30	[39]
PTMP	MB	5	64.5	8	[40]
Titania-incorporated polyamide	MB	6	43	30	[41]
PDDACD	MB	8-9	180	30	[42]
Polyzwitterionic resin	MB	7	14.9	-	[43]

based on the experimental data are listed in Table 2. By comparison of the $Q_{e.cal}$ (Q_e calculated by kinetic models) and $Q_{e.exp}$ (Q_e obtained by experiments) value, correlation coefficient (\mathbb{R}^2) and standard deviation (S.D.), adsorption process of TiO₂, PANI and PANI/TiO₂ for MB all fitted best with the pseudo-second-order model. It was indicated that chemical adsorption was the main adsorption controlling mechanism. However, the \mathbb{R}^2 value of pseudo-first-order model for TiO₂ was also higher ($\mathbb{R}^2 = 0.9995$), and the S.D. values was relatively low, showing that both chemical and physical adsorption participated crucially in the adsorption process. As the PANI was on the surface of PANI/TiO₂, adsorption process of PANI/TiO₂ for MB was similar to that of PANI, which are mainly chemical adsorption. The equilibrium adsorption capacities of three samples for MB followed the order: TiO₂ > PANI/TiO₂ > PANI under this condition.

To further study the rate control step of the whole adsorption process, the adsorption kinetic data of three adsorbents were fitted to Weber-Morris model(eq. S10) [48] and Boyd's film-diffusion model (Eq. S11) [49]. The results and parameters are listed in Fig. S12 and Table 2. From Fig. S12a, the adsorption process can be divided into three adsorption stages: membrane diffusion, particle diffusion and porous adsorption. In the whole adsorption process of TiO₂ for MB, there was almost no diffusion resistance. However, the adsorption rates of PANI and PANI/TiO₂ for MB were both significantly limited during membrane diffusion and particle diffusion stages. The internal diffusion rate declined more obviously than the membrane diffusion rate implied by the value of K_{WM} , which may be ascribed to the narrowed diffusion channel, increased electrostatic repulsion on the surface of the adsorbent, and decreased concentration of MB.

As for Boyd's film-diffusion model, if the plot is linear and cross the origin, the intra-particle diffusion is the main limiting factor of the adsorption rate; otherwise, liquid membrane diffusion or chemical reaction controls the adsorption rate [50]. From Fig. S12b, the fitting lines of all three adsorbents did not pass through the origin, confirming the adsorption rate was controlled by liquid membrane diffusion and chemical reaction.

Combining all the above analyses of kinetics data, the adsorption of MB on TiO₂ involved chemical and physical adsorption process, and external particle diffusion controlled the adsorption rate; the adsorption of MB onto PANI/TiO₂ was the same with that of PANI, and the adsorption rate was limited mainly by chemical adsorption, and intra-particle diffusion and membrane diffusion.

3.5. Adsorption isotherms

For further investigating the isotherms of MB adsorption onto PANI/ TiO₂, three adsorption isotherm models of Langmuir [51,52], Freundlich [53] and Temkin [54] were fitted with the adsorption equilibrium data.

Table 2

Adsorption kinetics parameters of MB onto TiO₂, PANI and PANI/TiO₂.

Pseudo-first-order model						
Sample	$k_1 ({\rm min}^{-1})$	$Q_{e.cal}$ (mg/g) (calculated)	$Q_{e.exp}$ (mg/g) (experiment)	R ²	S.D.	
TiO ₂ PANI PANI/TiO ₂	0.82 0.17 0.14	260.96 179.76 248.74	262.71 201.41 261.74	0.9995 0.8987 0.9477	1.75 21.65 13.00	
Pseudo-second-	order model					
Sample	$k_2(g/mg/min)$	$Q_e (mg/g)$	Q_e (experiment)	$k_2 Q_e^2(mg/g/min)$	R ²	S.D.
TiO ₂ PANI PANI/TiO ₂	0.0307 0.0015 0.0009	261.93 190.73 262.34	262.71 201.41 261.74	2106.24 55.05 64.74	0.9999 0.9732 0.9959	0.78 10.68 0.60
Simple Elovich e	equation					
Sample	A (a.u.)	B(mg/g)		R ²	S.D.	
TiO ₂ PANI PANI/TiO ₂	255.92 112.17 206.56	1.15 14.27 6.29		0.9020 0.9726 0.8668	0.54 3.43 23.67	
Weber-Morris n	nodel					
Sample		K_{WM} (mg/g/min ^{1/2})		C (mg/g)	R ²	
TiO ₂	First stage Second stage Third stage	1.0995 0.2835 0.0319		254.45 258.92 261.86	0.9748 0.8628 0.9596	
PANI	First stage Second stage Third stage	10.7736 2.7174 0.7985		106.41 153.09 179.95	0.9770 0.9861 0.9931	
PANI/TiO ₂	First stage Second stage Third stage	21.6375 3.8764 0.1786		113.11 215.64 257.21	0.9621 0.9421 0.6508	

The mathematical expressions and descriptions of the three isotherms models are detailed in Supplementary Material (Eq. S13-S15 in Appendix S4). The fitted curves and parameters of PANI, TiO_2 and $PANI/TiO_2$ are shown in Fig. 5 and Table S2.

From the conformance of experiment data and fitting curve, R^2 and S.D. values, it can be found that the adsorption of TiO₂ for MB at 298 K and 308 K was mainly accorded with the Freundlich model, indicating a heterogeneous adsorption. However, when the temperature increased to 318 K, no model could properly describe the adsorption of TiO₂, indicative of a changed adsorption mechanism. The adsorption data of PANI for MB fitted well with the Freundlich model, suggesting a heterogeneous adsorption. However, the adsorption process of PANI/TiO₂ for MB followed three isotherm models as: Temkin > Freundlich > Langmuir, implying that the process was chemically heterogeneous adsorption.

The 1/n of Freundlich model was <0.5 (except TiO₂ at 318 K), showing the adsorption of MB on three samples were preferential. K_L reflects the adsorption affinity; it can be seen that adsorption affinity of PANI/

 TiO_2 for MB was improved significantly compared with that of PANI and TiO_2 .

In the Temkin equation, the *b* was related with the maximum bond energy; the *b* value lower than 40 kJ/mol indicates a physical adsorption process. When the *b* is higher than 40 kJ/mol, it directs a chemical adsorption process [38]. According to the *b* values in Table S2, it can be found that the adsorption of MB on PANI/TiO₂ were mainly chemical adsorption process at 298 K.

3.6. Adsorption mechanism

3.6.1. FT-IR before and after adsorption

In order to investigate the surface chemical groups on adsorbents before and after adsorption, the FT-IR spectra of PANI, TiO_2 and PANI/ TiO_2 were analyzed (Fig. 6), and the assignments of characteristic peaks are listed in Table 3, S2, and S3.

According to Fig. 6a and Table S3, the characteristic absorption peaks of MB were observed after adsorption of MB onto TiO₂. The



Fig. 5. The fitting plots of isotherms models for MB adsorption on PANI, TiO2 and PANI/TiO2 at 298 K(a), 308 K(b) and 318 K(c) (Initial MB concentration: 5–2000 mg/L, pH at 9 for 12 h).



Fig. 6. FT-IR results of TiO₂(a), PANI(b) and PANI/TiO₂(c) before and after adsorption.

peaks at 1631 cm⁻¹ and 1554 cm⁻¹ corresponds to the hydroxyl and carboxyl group on TiO₂, respectively [55], were substituted by a characteristic absorption peak of MB. That might be the result of adsorption of MB on TiO₂ [56,57]. In addition, the peak of carboxyl group on TiO₂ at 1235 cm⁻¹ shifted to 1228 cm⁻¹, which further proved the carboxyl group as the MB adsorption site [22]. In the other hand, by comparing the characteristic absorption peaks of MB before and after adsorption, it was found that C-N characteristic peaks in the MB molecule shifted (1340 and 1397 cm⁻¹), showing that N atom in MB molecule might be the binding site with TiO₂.

Obvious difference can be observed in the FT-IR spectra of PANI before and after adsorption (Fig. 5b, Table S4). The peak at 1137 cm⁻¹ assigned to $Q = NH^+$ -B was replaced by the peak at 1168 cm⁻¹ for N = Q = N, implying that the PANI maintained the

Table 3 Assignments of characteristic peaks for PANI/TiO_2 before and after MB adsorption.

Wavenumber (cm ⁻¹)			Assignment	
PANI/TiO ₂	PANI/TiO2-MB	MB		
3421	-	3300-3500	O-H vibration	
3234	3227	-	N-H vibration	
2924	3047	3035	C-H vibration in benzene ring	
-	1669	1657	C=N stretching vibration	
-	-	1600,1537	Vibration of the aromatic ring skeleton	
1580	1597	-	C=C stretching vibration in quinone	
			ring	
1499	1499	-	C=C stretching vibration in benzene	
			ring	
-	-	1490	In-plane bending vibration of the	
			aromatic ring skeleton	
1444	1444	1444	C-H oscillation in methyl	
1376	1384	1397	C-N stretching vibration	
			C-H symmetric bending vibration in	
			methyl	
-	1326	1340	C-N stretching vibration	
1300	-	-	C-N stretching vibration in -NH-B-NH-	
1245	1228	-	C=O stretching vibratio	
1146	-	-	N-H stretching vibration in $Q = NH^+-B$	
-	1168、1172	-	N = Q = N stretching vibration	
-	1128	1140	C-S stretching vibration	
1045	-	1069	C-C stretching vibration	
-	1037	1038	C-S stretching vibration	
-	882	881	Up-and-down vibration of the aromatic	
			ring skeleton	
822	829	820	Out-plane bending vibration of C-H in	
			benzene ring	

emeraldine base, and no doping and de-doping happened during the adsorption [58]. The peaks at 1576 and 1499 cm⁻¹ corresponding to the quinone ring and the benzene ring shifted to 1592 and 1511 cm⁻¹, and the other characteristic peaks of PANI changed slightly, implying the chemical reaction was involved in the adsorption process [24]. According to the changes of the characteristic peaks of MB before and after adsorption, the adsorption occurred mainly on the N atom and aromatic ring in MB molecule; combining with the characteristic peaks shift of aromatic ring in PANI at 1643 cm⁻¹, the π - π stacking interaction between PANI and MB was confirmed [37]. The change of N-H characteristic peak at 3234 cm⁻¹ was the proof of the hydrogen-bond interaction [59].

The FT-IR spectra of PANI/TiO₂ before and after adsorption are displayed in Fig. 5c and Table 3. The peak corresponding to $Q = NH^+$ -B at 1146 cm⁻¹ disappeared, and new peaks corresponding to N = Q = N at 1168 and 1172 cm⁻¹ were observed after adsorption [60]; besides, the characteristic absorption peaks of quinone ring at 1580 cm⁻¹ shifted to 1597 cm⁻¹, and other characteristic peaks of PANI/TiO₂ also changed after adsorption, all indicating the chemical reaction participated in the adsorption. On the basis of the above analysis, it can be concluded that π - π stacking interaction and hydrogen-bond interaction happened in the adsorption process.

3.6.2. Surface properties after adsorption

In order to study the changes of surface properties on the adsorbents, the N₂ adsorption-desorption was carried on after adsorption of MB. The results are listed in Table 4. The specific surface area (S_{BET}) of three samples all decreased after adsorption of MB. For PANI, the pore volume (V) and pore radius (R) decreased after adsorption, showing that part of MB molecules de-

Table 4	
he surface properties of the samples.	

Samples	S_{BET} (m ² /g)	$V(cm^3/g)$	R(nm)
PANI/TiO ₂	11.894	0.0838	14.09
$PANI/TiO_2 + MB$	8.128	0.0582	14.32
TiO ₂	5.235	0.0290	11.09
$TiO_2 + MB$	2.667	0.0300	22.53
PANI	19.214	0.1175	12.23
PANI+MB	10.615	0.0643	12.11



Fig. 7. The schematic diagram of adsorption mechanism for MB on PANI/TiO₂ (a: hydrophobic interaction; b: π-π stacking interaction; c: hydrogen bonding; d:electrostatic interaction; D-N⁺: MB dye molecule with nitrogen ion).

posited in the pores of PANI during adsorption. The pore radius of TiO_2 increased after adsorption due to the pretreatment by NaOH solution, but the pore volume kept constant, which results from the adsorption of MB in the pore of the TiO_2 . As for the PANI/ TiO_2 , the pore volume decreased slightly, pore radius kept constant and the S_{BET} decreased significantly, showing that the adsorption occurred both on the surface and in the pores, which echoed the result that adsorption was controlled by intra-particle diffusion observed before.

The molecular dimension of MB was reported as: 1.43 nm (width) \times 0.61 nm (length) \times 0.40 nm (thickness) [5]. The theoretical monolayer adsorption capacity of PANI, TiO₂ and PANI/TiO₂ can be calculated by the following Eq. 3.

$$Q_D = \frac{S_{BET} / 1.43 \times 0.61 \times 10^{-18}}{N_A} \times M(mg/g)$$
(3)

where Q_D is the monolayer adsorption capacity calculated; $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$, is the Avogadro's constant; *M* is the molecular weight of MB, which is 373.9; S_{BET} is the specific surface area obtained by N₂ adsorption- desorption characterization.

The results are listed in Table S5. It can be found that the Q_D was far less than the Q_m , proving that the adsorption of MB on PANI, TiO₂ and PANI/TiO₂ were all multilayer adsorption.

On the basis of the above results, in the adsorption process of PANI/TiO₂ for MB, the PANI and TiO₂ parts exert different functions and mechanisms. The main adsorption sites of TiO₂ for MB were hydroxyl group and carboxyl group, and the adsorption was achieved by hydrogen bonding and electrostatic interaction. While as for PANI, the adsorption occurred mainly on imino, amino and benzene ring structures through hydrogen bonding, π - π stacking interaction and hydrophobic interaction.

The schematic diagram of adsorption mechanism for MB on PANI/ TiO_2 is demonstrated in Fig. 7.

4. Conclusion

PANI/TiO₂ synthesized in this study possessed out-standing adsorption performance for MB, such as high adsorption capacity (458.10 mg/g), wide pH applicability (pH 3–11), and good performance of regeneration. By the composition of PANI and TiO₂, PANI/TiO₂ exhibited more stable and higher regeneration efficiency than PANI and TiO₂; after 10 cycles, the adsorption efficiency

maintained above 99% using 0.1 mol/L HCl as stripping agent (100 mg/L MB solution). Adsorption equilibrium could be achieved within 120 min. The photocatalysis and molecular transformation of MB were both excluded, and the removal of MB was mainly attributed to adsorption. These superior performances indicated that PANI/TiO₂ was a kind of potential adsorbent for cationic dves. Further study on the adsorption mechanisms of PANI/TiO₂ for cationic dye MB revealed that multilayer chemical heterogeneous adsorption was the main adsorption mechanism. The adsorption rate of MB onto PANI/TiO₂ was limited by membrane diffusion and particle diffusion stages. During the adsorption of PANI/TiO₂ for MB, the adsorption of MB on TiO₂ part was mainly heterogeneous multilayer physisorption, on the hydroxyl and carboxyl sites; but the adsorption of MB onto PANI part was mainly heterogeneous multilayer chemical adsorption, and the interactions included hydrogen bonding and electrostatic interaction on amino site, and π - π stacking and hydrophobic effect on benzene ring site. The synergistic effect of PANI and TiO₂ increased the adsorption performance of PANI/TiO₂ for MB.

Given the study of the adsorption of anionic azo dyes (ARG), phosphate anion, and cationic dyes(MB), a potential widely-applied composite adsorbent: PANI/TiO₂ should be fully developed, and was worth further exploring.

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Appendix A. Supplementary data

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