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Synthesis of polyaniline/TiO₂ composite with excellent adsorption performance on acid red G

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A polyaniline-modified TiO₂ (PANI/TiO₂) composite was designed and synthesized *via* the *in situ* chemical polymerization of aniline monomer in the as-prepared TiO₂ solution. The composite was employed as a novel reusable adsorbent based on the unique doping–dedoping properties of polyaniline. Fourier transform infrared (FT-IR) spectra, scanning electron microscopy (SEM) and X-ray diffraction (XRD) were combined to characterize the chemical structure and morphology of PANI/TiO₂. The adsorption–desorption characteristics of polyaniline/TiO₂ (PANI/TiO₂) on Acid Red G (ARG) were further investigated. The prepared adsorbent possessed excellent adsorption and regeneration performances with the adsorption equilibrium time in about 5 min and the maximum adsorption capacity at 454.55 mg g⁻¹. The possible adsorption mechanism was proposed to be associated with the doping–dedoping behaviors of the PANI chain.

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Introduction

In recent years, the composites of conductive polymers and inorganic particles have been the focus of a great deal of research¹⁻⁵ due to their potential applications in chemical sensing, catalysis, energy storage, solar cells, and medical diagnosis.⁶⁻⁸ However, the application of this new type of materials as adsorbent in wastewater treatment, especially in the removal of dyes from printing and dyeing wastewater, is seldom reported.

Among conductive polymers (polyaniline, polypyrrole, polythiophene, *etc.*), polyaniline (PANI) has attracted considerable attention for its low cost, simple synthesis, excellent electrical conductivity, thermal stability, antioxidant properties, and so on.⁹⁻¹¹ The unique reversible electrochemical activity, large specific surface area, good stability and doping-dedoping reversibility, *etc.*,^{12,13} make the adsorption and desorption of ions on PANI possible by simple acid and alkali treatment. The use of polyaniline as adsorbent for dye removal has been reported recently.^{14,15} However, PANI, as a significant conductive polymer material with low mass density, is hard to be settled, which restricts the application as the adsorbent for the difficulty of recovery.

Titanium dioxide is one of the most widely studied metal oxide semiconductors in the research of inorganic materials because of its comparatively low cost, simple preparation, good stability, nontoxic nature, and photodegradation ability.¹⁶ Notably, the properties of insolubility and neutral pH_{pzc} value make TiO₂ an ideal adsorbent, and the adsorption capacity can

be developed over a broad range of pH.¹⁷ In addition, TiO₂ with large surface area^{18,19} carries a great deal of hydroxyl and carboxyl groups, which can interact with some pollutant molecules.^{20–22} Recently, the adsorption of TiO₂ on various dyes, such as acid orange 7,²³ porphyrin dyes,²⁴ Esin Y dye,²⁵ blue 21 dye²⁶ and so on^{27,28} was reported. However, pure TiO₂ has high selectivity on the adsorbates and poor regeneration capability.²⁹ Therefore, the improvement in the adsorption and regeneration capability of TiO₂ through modification with other substances has been one of the focuses. And the modified substances would not decrease its adsorption capacity,³⁰ for the incompleted –OH groups on TiO₂ do not fully contribute to the ion exchange process.

Thus, the composites of PANI and TiO₂ were proposed in this study to develop the merits of both organic and inorganic materials and to avoid the shortcomings of both. We synthesized PANI-modified TiO₂ (PANI/TiO₂) composite through the chemical oxidation of aniline in the as-prepared TiO₂ sol solution, and investigated its adsorption and regeneration properties for Acid Red G (ARG). It was found that PANI/TiO₂ composite exhibited excellent adsorption and regeneration properties even after several adsorption–desorption cycles. Furthermore, compared with some other adsorbents reported before, the PANI/TiO₂ composite adsorbent exhibited excellent adsorption performance for ARG and could reach the adsorption equilibrium in a very short time. Finally, a possible adsorption mechanism was proposed according to the doping– dedoping behaviors of the PANI.

Experimental

Materials

Aniline (99.5%, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was distilled twice under reduced pressure,

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and then stored in the dark at 0 $^{\circ}$ C protected by N₂. Acid Red G (ARG) was commercial grade and recrystallized twice before used. The structure of ARG is shown in Fig. 1. Other reagents were of analytical grade and used as received. The real effluent used in our study was derived from the printing and dyeing factory in Xi'an, China. The deionized water used for all the experiments was prepared by an EPED-40TF Superpure Water System (EPED, China).

Synthesis of the PANI/TiO₂ composite

The TiO₂ sol solution was prepared by the sol–gel hydrolysis¹⁵ in the mixture solution of HNO₃ (0.064 mol L⁻¹) and citric acid (0.1 mol L⁻¹), in which PANI/TiO₂ was formed by the chemical oxidative polymerization of aniline monomer. The typical process is as follows: the dispersed TiO₂ (2.35 g) in 100 mL mixture solution of HNO₃ (0.064 mol L⁻¹) and citric acid (0.1 mol L⁻¹) was magnetically stirred for 1.0 h. Afterwards, aniline (1.8 mL) monomer was added and stirred for 1 h. Then, ammonium persulphate (APS) solution (0.1 mol L⁻¹) was added and reacted for 8 h at ambient temperature. Finally, the composite was filtrated and washed with a large amount of deionized water and dried at 50 °C for 48 h. For comparison, the pure TiO₂ and PANI were prepared as above.

Characterization

XRD patterns of the samples were obtained by an X'Pert PRO MRD Diffractometer using Cu-K\alpha radiation ($\lambda = 1.5418$ Å). FT-IR spectra of samples were measured using the KBr pellet method on a BRUKER TENSOR 37 FT-IR spectrophotometer in the range of 4000-400 cm⁻¹. The Brunauer-Emmett-Teller surface area (S_{BET}) , total pore volume (V), and average pore radius (R) were determined by the ASAP2020 instrument using the Barrett-Joyner-Halenda (BJH) method. The thermogravimetric analysis (TGA) was performed on a Perkin Elemer TGA-7 in N2 flow at heating rate of 10 °C min⁻¹. The morphology was characterized by scanning electron microscopy (SEM, JSM-6700F, Japan; JJSM-6390A, JEOL instrument). The zeta potentials of adsorbents were measured with Malvern Zetasizer Nano ZS90, through adding 5 mg sample in 10 mL NaCl solution $(10^{-3} \text{ mol L}^{-1})$ at different pH values (adjusted with diluted HNO3 or NaOH solution).

Adsorption experiments

All adsorption experiments were carried out in the dark at ambient temperature. The suspension containing 500 mg L^{-1} ARG and PANI/TiO₂ adsorbent was magnetically stirred for a certain time and then centrifuged at 4000 rpm for 2 min. The



Fig. 1 Molecular structure of ARG.

supernatant was analyzed by the UV-Vis spectrophotometer (Agilent 8453) and the adsorption intensity peak at 503 nm corresponding to the azo group in acid red G was recorded, with which the concentration of ARG in solution can be calculated.

The influence of the pH on the adsorption capacities was investigated by adjusting the pH of ARG solution with NaOH or HNO₃ solution (pH = 1.0–13.0). Then the adsorbents were employed to treat ARG solutions with different pH. Due to the complexity of real effluent, the effect of ionic concentration on the adsorption was also conducted by adding NaCl (0–0.3 mol L⁻¹) into the 500 mg L⁻¹ ARG solution before the adsorption process. The optimal dosage of PANI/TiO₂ in the adsorption from 0.5 to 3.0 g L⁻¹. The thermodynamics of the prepared adsorbent was examined by changing the adsorption temperature from 10 to 35 °C.

The adsorption equilibrium of different concentrations of ARG (300, 500, and 700 mg L⁻¹) on PANI/TiO₂ was evaluated at 20 °C, with the optimal dosage of PANI/TiO₂ in 1 h. 10 mL of the mixture was fetched in the same time interval (10 min) and filtered for the UV-Vis spectrophotometer analysis at $\lambda_{max} = 503$ nm.

The adsorption rate R (%) and the amount of adsorbed dye on per gram of adsorbent (Q_t (mg g⁻¹)) in time t were calculated by the following equations, respectively:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

$$Q_t(\operatorname{mg} g^{-1}) = \frac{C_0 - C_t}{M} \times V$$
(2)

where: C_0 is the initial dye concentration (mg L⁻¹), and C_t is the concentration of dye adsorbed in time *t*; *V* is the solution volume (L) and *M* is the mass of the used adsorbent (g).

To determine the maximum adsorption capacity and the suitable isotherm model of the adsorbents for ARG (500–950 mg L^{-1}), the Langmuir and Freundlich isotherm models were selected to fit with the experimental data at 20 °C. Langmuir and Freundlich isotherms are described in the following equations, respectively:

$$\frac{C_{\rm eq}}{Q_{\rm eq}} \left(g \ \mathrm{L}^{-1} \right) = \frac{1}{Q_{\rm max} K_{\rm L}} + \frac{C_{\rm eq}}{Q_{\rm max}} \tag{3}$$

$$\lg Q_{\rm eq} \ ({\rm mg g}^{-1}) = \lg K_{\rm F} + n \lg C_{\rm eq} \tag{4}$$

where: Q_{eq} and Q_{max} (mg g⁻¹) are the equilibrium adsorption capacity and the maximum adsorption capacity, respectively; C_{eq} (mg L⁻¹) is the dye equilibrium concentration in the solution; K_L (L mg⁻¹) is a constant that relates to the heat of adsorption; K_F ((mg g⁻¹) (mg L⁻¹)⁻ⁿ) represents the adsorption capacity when C_{eq} equals 1; *n* represents the degree of dependence of adsorption on equilibrium concentration.

Regeneration experiments

Due to the reversible doping–dedoping chemistry of PANI and the neutral pH_{pzc} value of TiO₂, the as-prepared composites can

be regenerated by simple acid and alkali treatment theoretically. Therefore, 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} HCl solutions were used to treat the PANI, TiO₂ and PANI/TiO₂ 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 eqn (1) and (2).

The real ARG effluent was prepared by dissolving ARG (500 mg L^{-1}) into the real effluent instead of deionized water. The adsorption experiments of ARG effluent were the same as that of ARG solution.

Results and discussion

Characterization of the samples

The chemical structure of PANI/TiO2 was characterized by FT-IR spectroscopy in Fig. 2. The broadband centering at about 3300 cm⁻¹ could be assigned to the stretch vibration of O-H and N-H groups on the surface of TiO₂ and in the chains of PANI. In the spectrum of TiO₂, the wide peak at 500–700 cm^{-1} corresponds to Ti–O–Ti bending mode of TiO_2 .³¹ The bands at 1631, 1560, and 1237 cm⁻¹ are assigned to the O-H stretch vibration, the O-C=O asymmetric stretch vibration, and the C=O stretch vibration from the doped citric acid respectively. In addition, the peak at 1388 cm⁻¹ is assigned to the N–O stretching vibration introduced by nitrate ion from synthesis. In the spectrum of PANI, the characteristic peaks at 1577, 1502, 1301, and 827 cm⁻¹ are ascribed to the C=C stretching vibration of quinoid and benzenoid rings, C-N stretching of -NH-(C₆H₄)-NH- and C-H vibration out of benzene plane ring respectively.^{32,33} A wide peak at 1141 cm^{-1} assigned to the O=NH⁺-B adsorption peaks (where Q and B denote quinoid ring and benzene ring, respectively) is also observed.34 All the main characteristic bands of PANI and TiO₂ can be seen in the spectrum of PANI/TiO₂. The slight shift of characteristic peaks at 1577 and 1502 cm⁻¹ might be caused by the chemical interaction between the amine groups or the imine groups of the PANI chains and the TiO₂. The reaction occurred on the basis that titanium as transition metal has intense tendency to form coordination compound

 $H_{\text{AVEL}}^{\text{TiO}_{2}} = \frac{1}{2000} \frac{1}{200} \frac{1}{200} \frac{1}{200} \frac{1}{20$

Fig. 2 FT-IR spectra of TiO₂, PANI/TiO₂, and PANI samples.

with nitrogen atom in PANI macromolecule. This interaction as reported may weaken the bond strengths of C=N, C=C and C-N in PANI macromolecule,^{35,36} which can be confirmed by comparing the peak intensity of PANI and PANI/TiO₂.

According to Geniès,³⁷ the peak intensity ratio of quinoid and benzenoid structure (I_Q/I_B) in PANI is related to the degree of oxidation in the molecular chain. In Fig. 2, the I_Q/I_B ratio in the spectrum of PANI/TiO₂ and PANI were calculated by integrating the corresponding peaks area. A big change occurred for the I_Q/I_B ratio, 0.96 for PANI and 9.31 for PANI/TiO₂, suggesting significant increase of the oxidation degree in PANI molecule chain after the composition with TiO₂. The relation between the I_Q/I_B ratio and the adsorption would be discussed later.

Fig. 3 depicts the TGA curves of PANI/TiO₂, PANI and TiO₂. It can be seen that the weight loss of PANI occurred from 180 °C and lasted in the whole procedure with weight loss of 55 wt%. The weight loss of PANI/TiO₂ was similar to that of TiO₂ and showed a three-stage decomposition pattern. The first weight loss of PANI/TiO₂ and TiO₂ at temperature below 150 °C was attributed to desorption of water and anions inherited from the synthesis process.38 The major thermal event between 150-580 °C with about 18 wt% of weight loss may be assigned to the hydroxyl condensation dehydration on TiO2 and degradation of PANI. Above 300 °C, the weight of PANI/TiO₂ decreased faster than that of TiO₂, indicating the thermal degradation of PANI.³⁹ The last weight loss of 5.7 wt% above 580 °C in PANI/TiO₂ was attributed to further degradation of PANI. Comparing the TGA curve of PANI/TiO₂ and PANI, the as-prepared PANI/TiO₂ possessed higher thermal stability than PANI after the composition with TiO₂.

The morphologies of the prepared TiO_2 , PANI and PANI/TiO₂ were investigated by SEM in Fig. 4. It can be seen that PANI showed peculiar flake aggregation in Fig. 4a. Pure TiO_2 was spherical with uniform diameter under 500 nm (Fig. 4b). It can be seen from Fig. 4c that the composite PANI/TiO₂ was spherical with 1 µm of average diameter, which is much different with the PANI flake. It is indicated that the composition with TiO₂ could significantly change the morphology of PANI. The increase of



Fig. 3 TGA curves of TiO₂ and PANI/TiO₂.



Fig. 4 SEM images of the prepared (a) PANI, (b)TiO₂ and (c) PANI/TiO₂.

the average diameter of $PANI/TiO_2$ is possibly due to the aggregation of PANI on TiO_2 surface.

Fig. 5 shows the XRD patterns of the prepared TiO₂, PANI and PANI/TiO₂. For TiO₂, only a weak diffraction peak located at about 25.4° corresponding to the anatase TiO₂ (101) plane⁴⁰ was observed, indicating the amorphous state of TiO₂ prepared by the sol–gel method. The characteristic peaks of the doped PANI at around 20.0° and 25.7° attributed to the periodicity parallel and perpendicular to the polymeric chain^{41,42} were observed, suggesting obvious crystallinity in the prepared PANI. While in the pattern of PANI/TiO₂, the diffraction peak of the PANI at about 25.3° decreased significantly, suggesting the prepared adsorbent was amorphous. It was reported that when the polyaniline deposits on the surface of TiO₂ particle, the molecular chain of absorbed polyaniline is tethered and the degree of crystallinity decreases,⁴³ which is consistent with this study, and corresponds to the result of SEM.

Effects of pH and ionic concentration on adsorption

The effect of pH on adsorption capacities of the prepared PANI, TiO₂ and PANI/TiO₂ is shown in Fig. 6. It can be observed that TiO₂ exhibited extremely low capacity for dye removal in studied pH range. The adsorption rate of the PANI/TiO₂ was maintained more than 95% below pH 10, and was reduced to 55% at pH 13, indicating the adsorption of ARG occurred mainly on the PANI. In contrast, the plot of the PANI is similar to that of PANI/TiO₂ with lower adsorption rate (about 57% at pH lower than 10, and 0% at pH 13), suggesting that the composition of TiO₂ significantly increased the dye removal efficiency of PANI in the whole



Fig. 5 XRD patterns of the prepared TiO₂, PANI and PANI/TiO₂.



Fig. 6 Effect of pH on adsorption capacities of the prepared samples.

employed pH range. Actually, the performance difference of PANI and PANI/TiO₂ was mainly caused by the loss of PANI with low mass density which is hard to be settled, in the pre-treatment of the adsorbents. TiO₂ in the composition increased the settleability of the adsorbent thus increasing the adsorption and regeneration efficiency.

In order to analyze this phenomenon, zeta potentials of PANI, TiO_2 , and PANI/ TiO_2 at different pH values were measured and the results are shown in Fig. 7. At the zero zeta potential, the pH (labeled as pI) of PANI, TiO_2 , and PANI/ TiO_2 was 10.29, 2.13, and 3.37 respectively, suggesting that the composition of TiO_2 changed the zeta potentials of PANI. The change may be caused by two aspects: (1) the more negative surface potential of TiO_2 compared with the positive surface potential of the PANI, (2) the different dosages of TiO_2 (2.35 g)



Fig. 7 Zeta potentials of samples.

and PANI (1.83 g) in the composite. Due to these two aspects, the zeta potential of PANI/TiO2 was changed and different with that of PANI. As for PANI, at pH below pI, nitrogen atoms, mainly on the imine groups, which are easier to be protonated than the amine groups,44,45 are protonated, making the PANI carry positive charges. When the pH is above pI, PANI/TiO₂ is negatively charged due to competitive adsorption of OHanions on both imine and amine functional groups.46,47 When the adsorbents are positively charged, the anionic dye can be easily adsorbed through the electrostatic attraction. If the adsorbents are negatively charged, the electrostatic repulsion inhibits the adsorption of ARG molecules. The results of PANI and TiO₂ were consistent with the change of adsorption capacities at different pH. However, although the pI was 3.37, the prepared PANI/TiO₂ showed excellent adsorption efficiency in the pH range of 1-10, which indicated that the adsorption of PANI after composed with TiO₂ was not just dominated by electrostatic attraction.

Generally speaking, the real effluent from printing and dyeing factories is quite complex.⁴⁸ Therefore, the study on the effect of ionic concentration on the adsorption capacity was necessary and the result is shown in Fig. 8. It was found that the inhibition of ionic concentration on adsorption capacity was tiny. According to Zhang *et al.*,⁴⁹ on the one hand the ions can reduce the electrostatic attraction between the adsorbates and adsorbents, but on the other hand they can inhibit the electrostatic repulsion between the adsorbates. With these two aspects, the adsorption capacity of PANI/TiO₂ remained invariable with the change of ionic concentration.

Effects of adsorbent dosage and temperature on adsorption

In order to determine the optimal dosage of PANI/TiO₂ in application, the effect of PANI/TiO₂ dosage on the adsorption for ARG was studied and the result is shown in Fig. 9a. According to Fig. 9a, the adsorption efficiency increased consequently with the increase of dosage. The adsorption efficiency showed no obvious change when the dosage exceeded 2.0 g L^{-1} . As a result, the dosage of 2.0 g L^{-1} was chosen in the subsequent experiments.



Fig. 8 Effect of ionic concentration on the adsorption capacity of PANI/TiO₂. (NaCl (0–0.3 mol L⁻¹) was added into the 500 mg L⁻¹ ARG solution before the adsorption process).



Fig. 9 Effects of $PANI/TiO_2$ dosage (a) and temperature (b, insertion is a partial enlarged drawing) on the adsorption of ARG.

Fig. 9b shows the influence of temperature on adsorption at 10 °C, 20 °C and 35 °C. It can be seen that there is no significant fluctuation on the adsorption behaviors when the temperature was changed, which indicated that the adsorption of ARG on PANI/TiO₂ was temperature independent in the range of 10–35 °C.

Adsorption kinetics

Fig. 10 shows the adsorption kinetics of ARG on PANI/TiO₂. Fig. 10a depicts the influence of contact time on the adsorption of ARG on PANI/TiO₂ with different initial concentrations (300, 500, 700 mg L⁻¹). Evidently, the adsorption equilibrium of ARG on PANI/TiO₂ could be achieved in 5 min, which was much shorter than that of other adsorbents reported in literatures (listed in Table 3), indicating the as-prepared PANI/TiO₂ was a promising excellent adsorbent.

The adsorption kinetics of ARG onto PANI/TiO₂ was analyzed by the pseudo-first-order and pseudo-second-order models which are described in eqn (5) and (6), respectively. The results are illustrated in Fig. 10b and c.

$$\lg(Q_{\rm eq} - Q_t) = \lg Q_{\rm eq} - \frac{K_1}{2.303}t$$
(5)

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_{\rm eq}}^2 + \frac{t}{Q_{\rm eq}} \tag{6}$$

where *t* is the adsorption time (min), K_1 (min⁻¹), and K_2 (g mg⁻¹ min⁻¹) are the rate constants for the pseudo-first-order and pseudo-second-order models, respectively. Q_{eq} (mg g⁻¹) is the equilibrium adsorption capacity. Q_t (mg g⁻¹) is the adsorption capacity at *t* min.

The relevant parameters of the pseudo-first-order and pseudo-second-order models were calculated and are listed in Table 1. The validity of kinetic model can be evaluated by two



Fig. 10 Adsorption equilibrium curves of ARG onto $PANI/TiO_2$ (a); pseudo-first-order kinetic plot for the adsorption of ARG (b); and pseudo-second-order kinetic plot for the adsorption of ARG (c).

factors: the correlation coefficients (R^2) and the agreement of experimental data and calculated data.⁵⁰ It can be observed that the correlation coefficients of the pseudo-second-order model ($R^2 = 0.9999-1$) was more appropriate to describe the adsorption kinetics of PANI/TiO₂ for ARG than the pseudo-first-order model ($R^2 = 0.6342-0.7119$), which was consistent with most

adsorbents reported.^{51,52} Moreover, the calculated values of $Q_{\rm eq}$ from the pseudo-second-order model agreed well with the experimental data. Therefore, the adsorption kinetics of ARG on PANI/TiO₂ followed the pseudo-second-order model, indicating the multiple adsorption mechanism of the PANI/TiO₂ adsorbent with saturated sites.⁵³

Adsorption isotherms

Adsorption isotherms, as empirical models, are obtained from the experimental data by means of regression analysis and are often used to describe the equilibrium of the sorption at constant temperature. The most common isotherms are the Freundlich isotherm and the Langmuir isotherm. Fig. 11 depicts the linear forms of Langmuir and Freundlich adsorption isotherm models of PANI/TiO₂. Evidently, the degree of



Fig. 11 Liner forms for (a) Langmuir and (b) Freundlich isotherm model of ARG onto PANI/TiO_2.

Table 1 F	Parameters o	f the	pseudo-fi	rst-ord	er and	pseud	o-second	l-ord	er moo	de	ls
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	Pseudo first ord	er model		Pseudo second order model		
$C_0({ m mg~L}^{-1})$	K_1 (min ⁻¹)	$Q_{\rm eq} ({ m mg g}^{-1})$	R^2	$K_2 (g mg^{-1} min^{-1})$	$Q_{\rm eq} ({ m mg g}^{-1})$	R^2
300	0.0532	1.208	0.5318	0.1156	144.93	0.9999
500	0.1985	74.456	0.8589	0.0176	238.10	0.9999
700	0.1658	137.911	0.7638	0.0078	303.03	1

linearity of Langmuir adsorption isotherm model was better than that of Freundlich adsorption isotherm model. The parameters of Freundlich and Langmuir isotherm models are listed in Table 2. It was found that the adsorption behaviors of ARG on the PANI/TiO₂ followed the Langmuir adsorption isotherm, suggesting the adsorption process was a monolayer adsorption.

The dimensionless separation factor, R_L , which is used to study the applicability of Langmuir adsorption isotherm, is expressed in the following equations:

$$R_{\rm L} = \frac{1}{1 + bC_0} \tag{7}$$

where, C_0 is the initial concentration of ARG solution; *b* is Langmuir constant.

The adsorption process is irreversible when $R_{\rm L} = 0$, favorable when $0 < R_{\rm L} < 1$, linear when $R_{\rm L} = 1$, and unfavorable when $R_{\rm L} > 1.^{54,55}$ The $R_{\rm L}$ value here was calculated as 0.0041 for the adsorption of ARG, in the range of 0–1, indicating the process of ARG adsorbed on PANI/TiO₂ was favorable.

The largest adsorption amount of ARG onto PANI/TiO₂ composite derived from the Langmuir model was 454.55 mg g⁻¹, which was much higher than that of several other adsorbents reported in literatures (listed in Table 3). In addition, PANI/TiO₂ composites were also highlighted with the shorter equilibrium adsorption time than that of other adsorbents, suggesting that the PANI/TiO₂, a composite of conductive polymers and inorganic particles, possessed higher adsorption capacity for ARG dye, and was a promising adsorbent for the removal of anion dyes from wastewater.

Regeneration

Given the effect of pH and surface potential on the adsorption, the regeneration of $PANI/TiO_2$ was achieved by using NaOH

Table 2	Parameters of Langmuir a	and Freundlich	adsorption	isotherm
models				

Langmuir model				Freundlich model			
Q_{\max} (mg g ⁻¹)	$K_{\rm L}$ (L mg ⁻¹)	$R_{ m L}$	R^2	$K_{\rm F}(({ m mg~g^{-1}})\ ({ m L~mg^{-1}})^{-{ m n}})$	n	R^2	
454.55	0.25	0.0042	0.9985	206.2	0.18	0.9346	

As for the ARG solution, it can be observed that the adsorption rate slightly decreased, resulting from the incomplete stripping of ARG on PANI/TiO₂ and also the inevitable loss of adsorbents. In contrast, the adsorption efficiency for actual printing and dyeing wastewater containing 500 mg L⁻¹ ARG is less than that for pure ARG solution and showed a continuously decrease trend, which may be due to the complexity of actual dyeing wastewater. In spite of 8 cycles of adsorption/regeneration, the adsorption efficiency for ARG solution was still more than 80%. Additionally, for the real ARG effluent, the adsorption efficiency of PANI/TiO₂ was more than 77% after 8 times of regeneration. These results suggested that the PANI/TiO₂ composite can be regenerated by acid and alkali treatment and the adsorption stability were hardly affected.

For comparison, the regeneration of PANI and TiO_2 was also studied. According to the experimental result, the regeneration efficiency of PANI and TiO_2 were both much lower than that of PANI/TiO₂, almost negligible. For PANI, it resulted from the inevitable loss of the suspended PANI during desorption and activation process. And for TiO_2 , titanium hydrates as the main constituents of TiO_2 were very unstable to acid and would dissolve in 0.1 mol L⁻¹ HCl during the acid activation process,



Fig. 12 The adsorption/regeneration efficiency of PANI/TiO₂ for ARG solution and real ARG effluent.

Table 3	Adsorption	canacity	of PANI/TiO-	and other	adsorbents	for azo dves
	Ausoiblion	Capacity			ausorburus	

Adsorbents	Acid red dyes	$Q_{\max} \left(\text{mg g}^{-1} \right)$	$C_0 \left(\text{mg L}^{-1} \right)$	Equilibrium time (min)
PANI/TiO ₂	Acid red G	454.55	500	5
PPy/TiO_2 (ref. 2)	Acid red G	179.21	500	20
Activated carbon ⁵⁶	Acid red 97	52.08	30	30
CuFe ₂ O ₄ powder ⁵⁷	Acid red B	86.8	100	30
Montmori llonite ⁵⁸	Acid red G	171.53	300	60
Calcined-alunite ⁵⁹	Acid red 57	80.02	250	120
PANI-ES ⁶⁰	Alizarine cyanine green	56.00	175	60
PANI/iron oxide ⁶¹	Amido black 10B	61.72	80	150

A proposed adsorption mechanism

The possible adsorption mechanism may be related to the unique doping–dedoping behaviors of PANI in the PANI/TiO₂, where the ARG ions can be served as the dopants ions. In order to study the proposed mechanism of adsorption and subsequent removal of the dye ARG, the FTIR of the samples treated by different conditions were measured (Fig. 13). In Fig. 13, the PANI/TiO₂ is the prepared adsorbents without any treatment;



Fig. 13 FT-IR of Alkali-PANI/TiO₂, Acid-PANI/TiO₂, Ad-PANI/TiO₂, and PANI/TiO₂.

Table 4The I_Q/I_B ratio in the spectrum of the four samples							
Samples	$I_{\rm Q}/I_{\rm B}$	Adsorption rate (%)					
PANI/TiO ₂	9.31	44					
Alkali-PANI/TiO ₂	2.94	13					
Acid-PANI/TiO ₂	1.52	98					
Ad-PANI/TiO ₂	1.75	_					

Alkali-PANI/TiO₂ is the prepared adsorbent treated by alkali (0.1 mol L⁻¹ NaOH); Acid-PANI/TiO₂ is the Alkali-PANI/TiO₂ treated by acid (0.1 mol L⁻¹ HCl); and the Ad-PANI/TiO₂ is the Acid-PANI/TiO₂ after the adsorption for ARG.

From the Fig. 13, it can be found that there appeared a new peak at about 1047 cm⁻¹ in the FT-IR spectra of Ad-PANI/TiO₂ sample, which is attributed to S=O stretching vibration in ARG dye.⁶² We deduced that ARG dye may served as the dopant ions in the PANI chain during the adsorption, *i.e.* protonation, process. Here, the change of I_Q/I_B in different samples was studied because the doping degree of the PANI chain was reported to be associated with the I_Q/I_B ratio.^{63,64} The I_Q/I_B ratio in the spectrum of the four samples were calculated, and the results are listed in Table 4.

It can be seen from Table 4 that the I_Q/I_B ratio in prepared PANI/TiO₂ was the highest, indicating the largest content of quinoid units, which maybe result from the oxidation of APS whose hydrolysis products include H₂O₂. After the alkali treatment, the I_Q/I_B ratio decreased dramatically; the alkali treatment was considered as dedoping process. However, the value of the I_Q/I_B ratio (2.94) indicated the incomplete dedoping in the PANI chain. And then the I_Q/I_B ratio fell to 1.52 after the acid treatment, indicating the acid dual-doping resulted in the transfer of electron and the change of electron cloud.⁶⁵ No big change happened on the ratio after the adsorption. According to the doping behaviors of the PANI reported⁶⁵ and the results in Table 4, the possible adsorption process can be deduced as follows in Fig. 14.

As shown in the Fig. 14, the prepared PANI in the composites was mainly in the emeraldine oxidation state (PANI-ES) with dopant of nitrate and citrate ions on the imine nitrogen atoms in the preparation process (Fig. 14a). In this state, the adsorption rate (in Table 4) was only 44%, which happened mainly on the protonated imine N atoms with the replacement of nitrate and citrate ions by dye ions. When the composites was treated with NaOH, parts of nitrate and citrate ions were released by charge neutralization and the corresponding PANI chain backbone transformed from quinoid into benzenoid units⁴⁷ with the



Fig. 14 The proposed doping process and adsorption procedure.

 Table 5
 Surface property of different samples

Samples	$S_{\rm BET} \left({ m m}^2 { m g}^{-1} ight)$	$V\left(\mathrm{cm}^{3}\mathrm{g}^{-1}\right)$	<i>R</i> (nm)
TiO ₂	4.12	0.027	13.20
PANI	21.28	0.171	16.11
PANI/TiO ₂	4.69	0.043	18.50
Alkali-PANI/TiO ₂	3.055	0.018	11.91
Acid-PANI/TiO ₂	2.052	0.020	19.90
Ad-PANI/TiO ₂	30.61	0.067	4.39

decrease in the $I_{\rm O}/I_{\rm B}$ ratio; this process can also be considered as dedoping with NaOH. However, according to the Fig. 13 and Table 4, there still existed nitrate and citrate ions characteristic peaks (at 1388 and 1237 cm⁻¹) and the $I_{\rm O}/I_{\rm B}$ ratio was 2.94 for Alkali-PANI/TiO2. Therefore, it can be indicated that parts of quinoid units with dopant existed in the chain, and the structure of the PANI chain may be like Fig. 14b. The lowest adsorption rate at this state resulted from the small amount of protonated N atoms in this state, decreasing the substitution reaction of the counter ions on it. Then the chain of PANI was re-protonated with the excess HCl acid,66,67 resulting more protonated nitrogen atoms in the PANI chain and less quinoid units because of the electron transfer and the change of electron cloud. In the adsorption process, the re-protonated PANI chain attracted the anion dye through electrostatic adsorption, and the replacement of Cl⁻ ions with dye anions occurred because of the stronger electrostatic adsorption force and the concentration grads (see Fig. 14d and the FT-IR spectra of Ad-PANI/ TiO_2 in Fig. 13).

The surface properties of samples treated by different reagents were measured and the results are listed in Table 5. From Table 5, the prepared PANI/TiO₂ showed small S_{BET} , and the alkali and acid treatment decreased the S_{BET} , which may be the result of the chemical corrosion by alkali and acid. After the adsorption, the S_{BET} increased and the *R* decreased significantly, suggesting the aggregation of ARG on the adsorbents surface and into the pore. Interestingly, it can be indicated from Fig. 6, Tables 4 and 5 that the adsorption efficiency had nothing to do with the specific surface area, but showed a positive correlation with the pore radius, which was inconsistent with the traditional concept that adsorbent with larger surface area show high dye removal rate.

Conclusions

In this study, a novel composite adsorbent, PANI/TiO₂, was successfully synthesized. The formation of the PANI/TiO₂ composite was confirmed by XRD, FT-IR and SEM analysis. It was found that the PANI/TiO₂ was spherical structure with weak crystallinity. There existed certain interaction between PANI and TiO₂ according to the FT-IR. The TGA analysis showed that the amount of PANI composited in PANI/TiO₂ was close to 18 wt% and the PANI/TiO₂ possessed high thermal stability. According to the adsorption characteristics of ARG on PANI/TiO₂, it was found that PANI/TiO₂ composite performed

excellent adsorption capability after acid treatment, with adsorption efficiency of more than 90% for 500 mg L^{-1} ARG solution. Although the effect of ion concentration on adsorption was negligible, the influence of pH on the adsorption of PANI/ TiO₂ for ARG was significant. The adsorption stability experiments showed that in situ regeneration of PANI/TiO₂ was successfully achieved with NaOH as stripping agent, and HCl as activator. Adsorption equilibrium of PANI/TiO₂ for ARG could be achieved within 5 min. The adsorption kinetics of PANI/TiO₂ for ARG was interpreted well by the pseudo-second-order model, indicating the multiple adsorption mechanism of the PANI/TiO2 adsorbent with saturated sites. According to the Langmuir adsorption isotherm model, the adsorption process was a monolayer adsorption and the maximum adsorption capacity of ARG on PANI/TiO₂ was 454.55 mg g^{-1} . In spite of regeneration for 8 times, PANI/TiO2 still possessed excellent adsorption capacity for both the pure ARG solution and the real ARG effluent. It is expected that PANI/TiO₂ composites would have promising prospects on anion dye removal in wastewater treatment. The adsorption mechanism of the PANI/TiO₂ adsorbent was closely related to the doping-dedoping behaviors of the PANI chain on the nitrogen atoms, and may have nothing to do with the special surface area. The adsorption of ARG on the composite can be considered as the substitution reaction of the counter ions on the protonated N atoms.

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