



Effect of hydroxyl group of carboxylic acids on the adsorption of Acid Red G and Methylene Blue on TiO₂

Jiangtao Feng^a, Jinwei Zhu^b, Wei Lv^a, Jingjing Li^a, Wei Yan^{a,*}

^a Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, PR China

^b China Aerospace Science and Technology Corporation Forty-fourth Research Institution, Xi'an 710049, PR China

HIGHLIGHTS

- The surface chemical properties of TiO₂ was proportional to the used acids.
- The surface chemical properties impact the adsorption behaviors of TiO₂ on dyes.
- TiO₂ can be easily regenerated by a solvent operation and reused at least 5 times.
- Adsorption mechanism involves in electrostatic and electron acceptor–donor effect.
- Carboxylic acid impact the surface chemical properties of TiO₂ and their adsorption.

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ABSTRACT

While TiO₂ has generated great interest in the removal of organic pollutants in recent years, the effect of the surface chemical property of TiO₂ on the adsorption performance is unclear. Here, TiO₂ samples were prepared in succinic (without hydroxyl group), malic (with one hydroxyl group) and tartaric acid (with two hydroxyl groups) by hydrolysis method and labeled as SU-TiO₂, MA-TiO₂ and TA-TiO₂, respectively. Their adsorption performance for anionic dye-Acid Red G (ARG) and cationic dye-Methylene Blue (MB) was investigated. The adsorption study indicates that the adsorption amount of ARG or MB was proportional to the alkalinity or the acidity, which is related to the number of hydroxyl group of the used acids, of the as-prepared TiO₂. Therefore, SU-TiO₂ displayed the largest adsorption capacity for ARG, while TA-TiO₂ had the highest adsorption capacity for MB. Furthermore, TA-TiO₂ can be reused at least 5 times without losing its adsorption capacity. The results indicate that the adsorption mechanism involves in the electrostatic interaction and the electron acceptor–donor interaction.

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1. Introduction

Adsorption has been proved to be an efficient approach for the removal of dyes from wastewater, due to its low capital investment, abundant raw material source, simplicity in design and operation, and non-toxicity. Many dyes with varied properties co-exist in wastewater, which influence the adsorption behavior of the used adsorbent. The different adsorption capacities are mainly affected by the textural properties and nature of the adsorbent, especially the chemical nature. The related studies have been conducted on activated carbons. The amount and nature of the oxygen-containing functional groups can affect the adsorption capacity of the activated carbon [1–5]. The liquid phase oxidation (HNO₃ or H₂O₂) generates a large amount of acidic surface groups,

e.g. carboxyl, anhydride, lactone and phenol groups. The NH₃ reduction and thermal treatments introduce the basic character onto activate carbons, for example carbonyl, pyrone and chromene groups. The activated carbon with acid groups would prefer to adsorb basic materials, while those with basic groups tended to adsorb acid materials. Therefore, the surface chemical nature of the activated carbon plays an important role in its adsorption performance.

Recently, many studies have focused on the adsorption of TiO₂ for its low cost, simple preparation, good stability and non-toxic nature [6–11]. Belessi et al. [7] claimed that the TiO₂ they prepared had the adsorption capacity of 86.96 mg/g for Reactive Red 195. Janus et al. [10] found that the adsorption capacity of carbon-modified TiO₂ for Direct Green 99 was enhanced to 96.77 mg/g, which was more than that of the unmodified TiO₂. Vu et al. [12] suggested that the adsorption capacity of Cu(II) on anatase mesoporous TiO₂ nano-fibers prepared via electrospinning was about 12.8 mg/g.

* Corresponding author. Tel./fax: +86 029 82664731.

E-mail address: yanwei@xjtu.edu.cn (W. Yan).

Besides, a little attention was paid to the effect of TiO₂ chemical property on its adsorption ability. Li et al. [13] pointed out that the isoelectric point of TiO₂ treated with HCl solution was larger than that of TiO₂ without treatment, which further affected the removal efficiency for oleic acid and oleylamine of the treated TiO₂ and un-treatment TiO₂. Wang et al. [14] indicated that the surface charge of TiO₂ was changed by modified with Nafion, and the Nafion-coated TiO₂ exhibited different adsorption capacity for Reactive Red 22 and Basic Red 2 from the original TiO₂. However, the further study on the influence mechanism of the surface chemical property to the adsorption performance of TiO₂ is favor to its application in the removal of pollutants in water.

Reports indicate that TiO₂ prepared in carboxylic acids can possess different crystal structure [15–17]. However, the effect of the surface chemical property of TiO₂ on the photocatalytic or adsorption performance was not investigated in detail. Herein, we prepared the TiO₂ particles in diverse carboxylic acid systems with different numbers of hydroxyl group. Then, the differences of the surface chemical property in TiO₂ prepared within the selected carboxylic acids were investigated. Furthermore, the effect of the as-prepared TiO₂ surface chemical property on the adsorption capacities for Methylene Blue and Acid Red G were studied.

2. Experimental

2.1. Materials

Anionic dye Acid Red G (ARG, 509.43 g/mol) was commercial grade and re-crystallized before used. Cationic dye Methylene Blue (MB, 319.86 g/mol) was purchased from Beijing Chemical Reagent Co., China and used as received. The structures of ARG and MB are shown in Fig. 1. Succinic acid, malic acid and tartaric acid were purchased from Sinopharm, China, and their structures are displayed in Fig. 2. FeCl₃·6H₂O, NaOH, HCl, n-propanol and tetrabutyl titanate (TBOT, 98%) are of analytical grade. The deionized water used for all experiments is obtained from the EPED-40TF Super-pure Water System (EPED, China).

2.2. Synthesis of different acid modified TiO₂

TiO₂ powder was synthesized by hydrolysis method [18,19]. In a typical process, a mixture of TBOT and n-propanol (the volume ratio is 5:2) was added into 200 mL carboxylic acid solution (0.16 mol/L) with magnetic stirring for 2 h at 65 °C. Then the suspension was stirred for another 12 h at ambient temperature. Finally, the white solid was filtrated and washed several times with water until the pH value of the washing liquid became neutral, and then dried at 50 °C for 24 h. The prepared TiO₂ samples were named as SU-TiO₂, MA-TiO₂ and TA-TiO₂ according to the carboxylic acids (succinic, malic and tartaric acids) used in the synthetic process, respectively.

2.3. Characterization

Fourier Transform Infrared spectra (FT-IR) of the TiO₂ samples were conducted by the KBr pellet method on BRUKER TENSOR 37

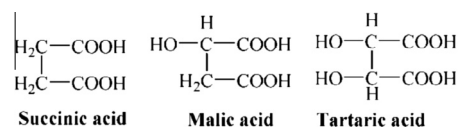


Fig. 2. Molecular structures of succinic, malic and tartaric acids.

FT-IR spectrophotometer in the range of 4000–400 cm⁻¹. BET surface area (*S*_{BET}), total pore volume (*V*) and average pore radius (*R*) were measured at 77 K using Builder SSA-4200 (Beijing, China). The thermogravimetric (TG) analyses were performed on Setaram Labsys Evo in N₂ flow at a heating rate of 10 °C/min.

Zeta potentials were tested with Malvern Zetasizer Nano ZS90. Samples for zeta potential measurement were prepared by adding 5 mg of TiO₂ in 10 mL NaCl solution (10⁻³ mol/L) at different pH values from 2 to 12 (adjusted with diluted HNO₃ or NaOH solution).

The acidity of the samples was estimated by mixing 0.05 g of TiO₂ with 25 mL NaOH (0.05 mol/L) in a closed flask, and shaken for 24 h at 25 °C. Then the suspension was centrifuged and the supernatant was titrated by a 0.05 mol/L HCl solution, and the HCl consumption (mL) was recorded. The alkalinity was obtained by a similar procedure where a 0.05 mol/L HCl solution was put in contact with the samples and 0.05 mol/L NaOH as the titration solution. The NaOH consumption (mL) was also recorded.

Temperature programmed desorption (TPD) profiles were obtained by Builder PCA-1200 (Beijing, China). The mass of the sample was 300 mg, the flow rate of the helium carrier gas was 30 mL/min, and the temperature program was from room temperature to 700 °C at a heating rate of 10 °C/min. The off-gas from the TPD was collected by a gas sampling bag and then tested by gas chromatogram (SP-2100, Beijing Beifeng-Ruili Analytical Instrument Co., Ltd., China) through injection into a packed column (HayeSep D, 2 m × 3 mm) carried by helium gas (10 mL/min). The inlet temperature was 60 °C, the oven temperature was 100 °C for 4 min. And the temperature of the TCD detector was 150 °C.

2.4. Adsorption experiments

The adsorption experiment of ARG or MB was evaluated by shaking the mixture of ARG or MB solution with as-prepared TiO₂ at 25 °C. Then the suspension was centrifuged at 4000 rpm for 5 min. The supernatant was analyzed by the UV-Vis spectrophotometer (Agilent 8453) to evaluate the adsorption capacity of TiO₂. The absorbance values of ARG and MB solution were read at the wavelength of 503 and 665 nm, respectively.

The adsorption rate *R* (%) and the amount of dye molecules adsorbed onto the as-prepared TiO₂ *Q_t* (mg/g) in a certain time *t* were calculated from Eqs. (1) and (2), respectively:

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

$$Q_t = \frac{C_0 - C_t}{M} \times V \quad (2)$$

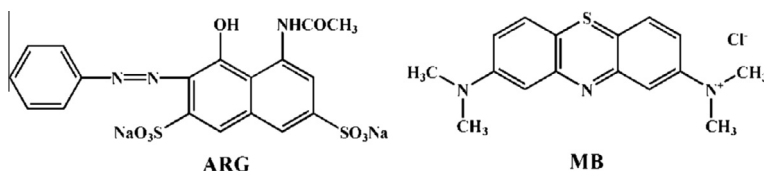


Fig. 1. Molecular structures of ARG and MB.

Table 1
Textural property of the TiO₂ samples.

Samples	<i>S</i> _{BET} (m ² /g)	<i>V</i> (cm ³ /g)	<i>R</i> (nm)
SU-TiO ₂	238.57	0.30	2.32
MA-TiO ₂	26.34	0.096	6.43
TA-TiO ₂	8.26	0.067	7.31

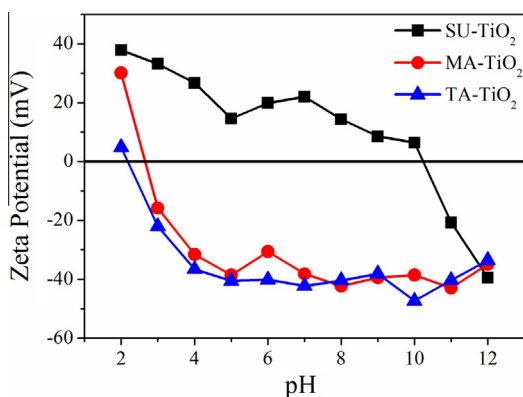


Fig. 3. Zeta potential analyses of SU-TiO₂, MA-TiO₂ and TA-TiO₂.

where *C*₀ (mg/L) is the initial concentration of the dye solution; *C*_{*t*} (mg/L) is the residual concentration of the dye solution at time *t* (min); *V* (L) is the solution volume, and *M* (g) is TiO₂ mass.

The adsorption equilibrium of ARG or MB (200, 300 and 500 mg/L) was evaluated at 25 °C. Adsorption isotherms of ARG or MB at 25 °C were obtained by mixing different concentrations (50–1200 mg/L) of ARG or MB solution with 2 g/L of as-prepared TiO₂, which was shaken for 120 min in dark. The Langmuir and Freundlich isotherm models were described according to Eqs. (3) and (4), respectively:

$$Q_t = \frac{Q_{\max} K_L C_t}{1 + K_L C_t} \quad (3)$$

$$Q_t = K_F C_t^{1/n} \quad (4)$$

where *Q*_{max} (mg/g) is the maximum monolayer molecular adsorption capacity onto the adsorbent in Langmuir isotherm model; *K*_{*L*} (L/mg) and *K*_{*F*} (L/g) are the constants of Langmuir and Freundlich isotherm models, respectively. 1/*n* represents the degree of dependence of adsorption on equilibrium concentration in Freundlich isotherm model.

Besides, the dimensionless separation factor *R*_{*L*}, which is an essential characteristic of the Langmuir model to reflect the favorability of an adsorption process, is expressed as:

$$R_L = \frac{1}{1 + K_L C_m} \quad (5)$$

where *C*_{*m*} (mg/L) is the maximum initial concentration of ARG or MB in solution.

Table 2
The FT-IR absorptions and their assignments [21,22].

Adsorbent	Wavenumber (cm ⁻¹)						
	<i>ν</i> (C=O)	<i>δ</i> (O–H)	<i>ν</i> _{as} (COO ⁻)	<i>ν</i> _s (COO ⁻)	<i>ν</i> (C–OH)	<i>ν</i> (C–C)	Ti–O
SU-TiO ₂	1715	1620	1532	1402	–	1065	400–1000
MA-TiO ₂	1730	1635	1550	1389	1105	1050	
TA-TiO ₂	1715	1626	1570	1422	1130	1078	

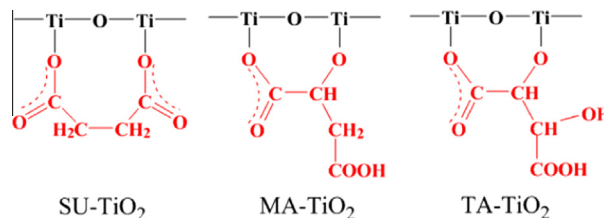


Fig. 4. Proposed coordination structures between carboxylic acids and TiO₂.

3. Results and discussion

3.1. Characterizations of the as-prepared TiO₂ samples

3.1.1. Physical characterization

The textural characterizations of SU-TiO₂, MA-TiO₂ and TA-TiO₂ are presented in Table 1. SU-TiO₂ has the largest *S*_{BET} and total pore volume (*V*), while the average pore radius (*R*) of TA-TiO₂ is the largest. This suggests that the carboxylic acids largely impact the textural properties of the as-prepared TiO₂ adsorbents, which would further affect the adsorption performance of the as-prepared TiO₂.

3.1.2. Surface chemical property characterization

The zeta potential value of the as-prepared TiO₂ samples is shown in Fig. 3, where the isoelectric point (pH_{iep}) is the pH value when the zeta potential value is equal to zero. The pH_{iep} values of SU-TiO₂, MA-TiO₂ and TA-TiO₂ are about 10.2, 2.7 and 2.1, respectively. This suggests that the surface of MA-TiO₂ and TA-TiO₂ has acid groups, while that of SU-TiO₂ is alkaline and further indicates that succinic, malic and tartaric acid can complex with TiO₂. It can be further concluded that both carboxyl groups of succinic acid are involved into the coordination reaction, whereas two carboxyl groups of malic and tartaric acids partly complex with TiO₂ because the acid groups are from the carboxyl groups.

The FT-IR spectra of the as-prepared TiO₂ samples were examined (Fig. S1), and their assignments are listed in Table 2. The characteristic peaks of carboxylate appear in the FT-IR spectra of all the TiO₂ samples, indicating succinic acid, malic acid and tartaric acid coordinated with TiO₂. The different antisymmetric (*ν*_{as}) and symmetric (*ν*_s) stretching absorptions of the carboxylate group are shown in SU-TiO₂, MA-TiO₂ and TA-TiO₂. The values of $\Delta\nu(\text{COO}^-) = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$ for SU-TiO₂, MA-TiO₂ and TA-TiO₂ are 130, 161 and 148 cm⁻¹, respectively. The coordination of carboxylic acids has three common modes via the carboxylate group, which can be distinguished by examining the value of $\Delta\nu(\text{COO}^-)$ [20–22]. The value of $\Delta\nu$ centering at 100–200 cm⁻¹ indicates a bridging structure. This implies that succinic acid, malic acid and tartaric acid can form bridging complex with TiO₂. In combination with the results of zeta potential analyses, succinic acid mainly coordinates with TiO₂ through two carboxyl groups. For malic acid or tartaric acid, it largely reacts with TiO₂ through a carboxyl group and a hydroxyl group. Therefore, the proposed coordination structures between carboxylic acids and TiO₂ are displayed in Fig. 4.

The data in Table 3 reflects the TG analyses of the as-prepared TiO₂ samples (Fig. S2). The first stage below 120 °C is generally attributed to the loss of physically adsorbed water [23]. The second stage between 120 and 200 °C is probably due to the loss of chemically adsorbed water [23,24]. TA-TiO₂ shows the largest weight loss in this stage, followed by MA-TiO₂ and SU-TiO₂, which indicates that TA-TiO₂ possesses the most hydroxyl groups. A likely explanation is that TA-TiO₂ exhibits the most hydroxyl groups because of tartaric acid with two hydroxyl groups. The third stage between 200 and 550 °C is probably assigned to the decomposition of the carboxylic acids. Furthermore, the weight loss in the range of 200–320 °C is mainly originated from the decomposition of the uncoordinated carboxyl groups, and that in the range of 320–550 °C is mainly due to the decomposition of the coordinated carboxylate groups. Table 3 displays the amount of hydroxyl and carboxyl groups in TA-TiO₂, MA-TiO₂ and SU-TiO₂. These data suggest that the hydroxyl and carboxyl groups of the as-prepared TiO₂ rise with the increasing number of hydroxyl group of the used carboxylic acid.

Fig. 5 shows the TPD spectra of the as-prepared TiO₂ samples. The peak at low temperature results from the decomposition of the carboxylic groups and that at high temperature is due to the decomposition of the carbonyl groups [1–3]. The area of the peak at low temperature of TA-TiO₂ is largest. This indicates that TA-TiO₂ contains the largest amount of carboxylic groups and it will produce more CO₂ in the TPD process. Besides, SU-TiO₂ has the biggest area of the peak at high temperature, illustrating that SU-TiO₂ contains more carbonyl groups and it will produce more CO in the TPD process. This result is also proved by the gas chromatograms of the TPD off-gases (Fig. S3). It further suggests that both of the carboxyl groups of succinic acid take part in the coordination with TiO₂ to form SU-TiO₂, while the carboxyl groups of malic or tartaric acid partly coordinate with TiO₂ to form MA-TiO₂ and TA-TiO₂, respectively.

The acidity/alkalinity of SU-TiO₂, MA-TiO₂ and TA-TiO₂ are measured by acid-base titration. The acidities of SU-TiO₂, MA-TiO₂ and TA-TiO₂ are 1.6, 3.0 and 3.8 mmol NaOH/g, respectively. The alka-

linities of SU-TiO₂, MA-TiO₂ and TA-TiO₂ are 2.4, 1.3 and 0.8 mmol HCl/g, respectively. Therefore, TA-TiO₂ and MA-TiO₂ have stronger acidity owing to the uncoordinated carboxyl groups. SU-TiO₂ owns the highest alkalinity, due to the carbonyl groups.

Finally, the carboxylic acids with or without hydroxyl groups impact the chemical properties of the as-prepared TiO₂. The acidity of the TiO₂ sample rises with the increasing number of hydroxyl groups of the used carboxylic acids, while the alkalinity decreases with the increasing number of hydroxyl groups. TA-TiO₂ and MA-TiO₂ have an acidic surface, and SU-TiO₂ has a basic surface. TA-TiO₂ possesses the maximum hydroxyl and carboxyl groups, and then MA-TiO₂. SU-TiO₂ has many carbonyl groups in their surface.

3.2. Adsorption experiments

3.2.1. Effects of pretreatment solution pH on the adsorption capacity

The adsorption capacities of the as-prepared TiO₂ samples are altered when they were pretreated with aqueous solution in varied pH value (adjusted by 1.0 mol/L HCl or NaOH solution), as shown in Fig. 6. The adsorption amount of ARG rises with the pH decrease and reaches the largest at the pH of 1, suggesting that ARG can be easily adsorbed on the acid-treated TiO₂. While the adsorption amount of MB increases with the pH increase and reaches the largest at the pH of 13, indicating that MB can be easily adsorbed on the alkali-treated TiO₂. However, the adsorption variation trend of SU-TiO₂, MA-TiO₂ and TA-TiO₂ for ARG and MB is similar, respectively.

Wang et al. [14] pointed out that the surface chemical properties can be changed when it is modified by organic materials. For example, the Nafion modified TiO₂ has negatively charged surface for the anionic sulfonate groups in the Nafion coordinated with the positively charged surface groups of TiO₂ and the backbone of Nafion presented on the outer planes in the aqueous solution. In this study, the carboxylic acids modified TiO₂ samples have different surface charges compared with the pure TiO₂ (pH_{iep} = 6.8) [25]. According Wang's viewpoint, the carboxylic acids modified TiO₂ samples with anionic carboxyl groups on the outer planes of the material will have negatively charged surface, while the TiO₂ sample only with alkyl groups on the outer planes of the material will have positively charged surface. This result is also testified by the zeta potential analyses, the pH_{iep} values of SU-TiO₂, MA-TiO₂ and TA-TiO₂ are about 10.2, 2.7 and 2.1, respectively. Thereby, the surface of MA-TiO₂ or TA-TiO₂ is positively charged in the pH of 1–3, and then it can adsorb ARG through the electrostatic attraction, while it shows weak adsorption capacity for MB due to the electrostatic repulsion. MA-TiO₂ and TA-TiO₂ carry negative charges when the pH is larger than 3. Hence, they exhibit poor ARG adsorption ability due to the electrostatic repulsion and possess enhanced MB adsorption capacity owing to the electrostatic attraction. However, for SU-TiO₂, it is positively charged in the pH of 1–10 and negatively charged in the pH of 10–13. Thus, SU-TiO₂ displays improving adsorption ability for MB when pH is only larger than 10. Besides, the positive charges of SU-TiO₂, MA-TiO₂ and TA-TiO₂ increase with the declining pH value, so they have the largest adsorption capacity for ARG at pH of 1. Conversely, they can carry more negative charges when pH increases to 13, so they possess the largest adsorption capacity for MB at pH of 13. Finally, the prepared TiO₂ adsorbents are pretreated with 0.1 mol/L of HCl to adsorb ARG solution and pretreated with 0.1 mol/L of NaOH to adsorb MB solution in the following experiments.

3.2.2. Adsorption equilibrium

According to the influences of contact time on the adsorption of ARG and MB with various initial concentrations onto SU-TiO₂, MA-TiO₂ and TA-TiO₂ (Fig. S4), the adsorption process can be divided into three stages. The adsorption rate is fast in the first stage

Table 3
Mass loss of SU-TiO₂, MA-TiO₂ and TA-TiO₂ at different stage.

Adsorbent	Mass loss (wt%)			
	<120 °C	120–200 °C	200–320 °C	320–550 °C
SU-TiO ₂	3.67	2.79	1.96	7.25
MA-TiO ₂	7.84	8.58	10.74	8.19
TA-TiO ₂	6.42	10.14	14.56	5.23

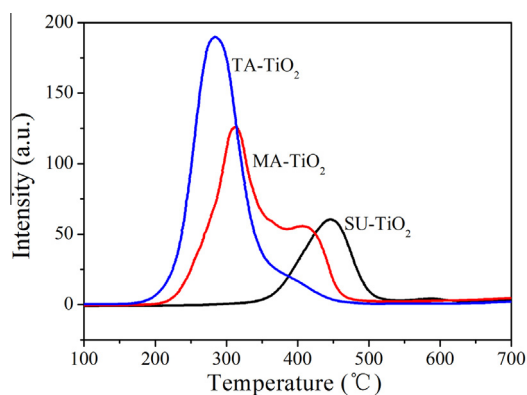


Fig. 5. TPD spectra of SU-TiO₂, MA-TiO₂ and TA-TiO₂.

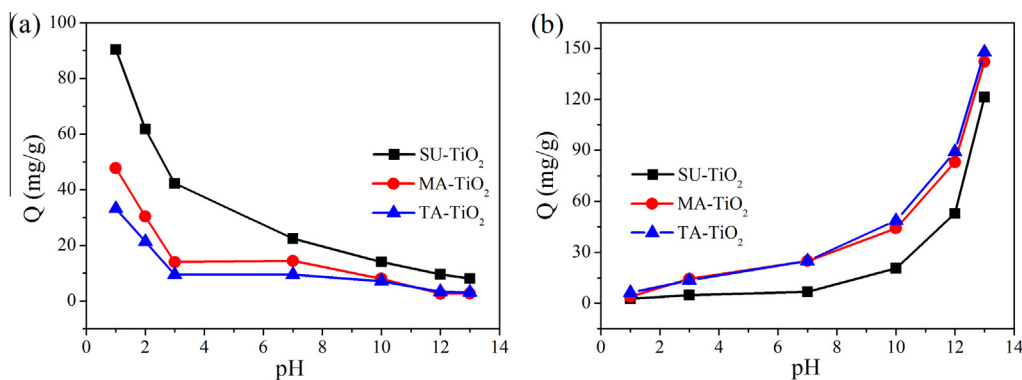


Fig. 6. Effects of pH of the pretreatment solution on the adsorption capacities of SU-TiO₂, MA-TiO₂ and TA-TiO₂ for (a) ARG and (b) MB, respectively.

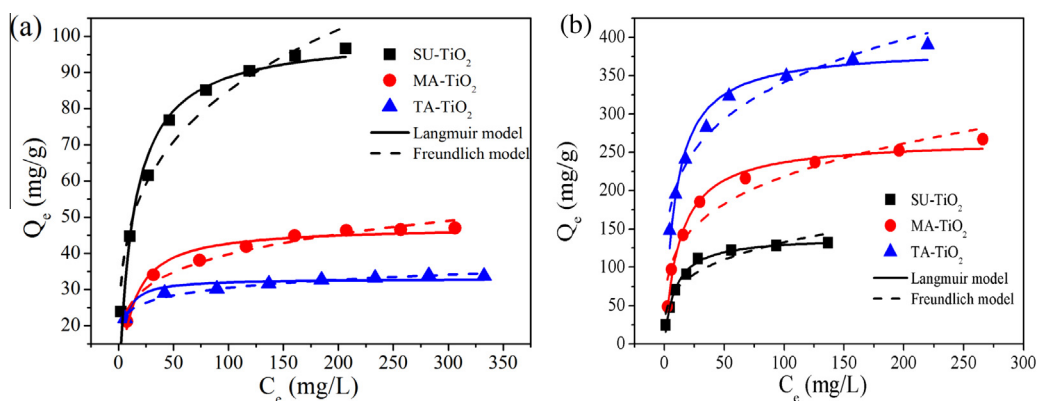


Fig. 7. Langmuir and Freundlich adsorption isotherm models of ARG (a) and MB (b) on SU-TiO₂, MA-TiO₂ and TA-TiO₂, respectively.

(0–10 min). In the time of 10–60 min, the adsorption rate is gradually reduced. After 60 min, the adsorption process reaches the adsorption equilibrium. Therefore, it is feasible to choose 120 min as the adsorption time in the following adsorption experiments.

Besides, the adsorption amount of ARG or MB on SU-TiO₂, MA-TiO₂ and TA-TiO₂ increases with the initial concentration of ARG or MB. However, it is observed that the increment of the adsorption amount of ARG on MA-TiO₂ and TA-TiO₂ is far less than that of MB. This suggests that the adsorption capacities of MA-TiO₂ and TA-TiO₂ for MB are higher than that for ARG.

3.2.3. Adsorption isotherm

In order to describe the interaction between adsorbate and adsorbent, the adsorption isotherm at 25 °C was investigated. Langmuir and Freundlich adsorption isotherm models for SU-TiO₂, MA-TiO₂ and TA-TiO₂ are displayed in Fig. 7. The corresponding data are listed in Table S1. Comparing to the correlation coefficient (R^2), Langmuir model is more fitted for describing the adsorption process, which suggests that the adsorption sites of the TiO₂ adsorbents are finite and the adsorption process is a monolayer adsorption reaction. Besides, the values of R_L are found to be in the range of 0–1, and the values of $1/n$ are centered in the range of 0.1–0.5, indicating that the adsorption processes are favorable.

3.2.4. Regeneration

TA-TiO₂ has the largest adsorption capacity for MB (386.56 mg/g), so it is chosen as the target adsorbent to investigate the regeneration performance. According to the analysis of the pH effect section, it is available that MB can be desorbed from TA-TiO₂ by acid

treatment. Therefore, 0.1 mol/L HCl is chosen as the desorption agent. Then, 0.1 mol/L NaOH is employed as the active agent. The activated TA-TiO₂ is employed as the adsorbent in 300 mg/L of MB solution. The regeneration result of TA-TiO₂ is shown in Fig. 8. It is observed that the removal efficiency of TA-TiO₂ is still higher than 95% after adsorption–desorption for 5 cycles, suggesting that TA-TiO₂ has an excellent regeneration performance.

3.3. The correlation between the properties and adsorption capacities of TiO₂

It is noted that the adsorption capacities of the as-prepared TiO₂ samples for MB are not proportional to their specific surface area S_{BET} . This implies that the specific surface area (physical property) is not a key factor for the adsorption ability of the TiO₂.

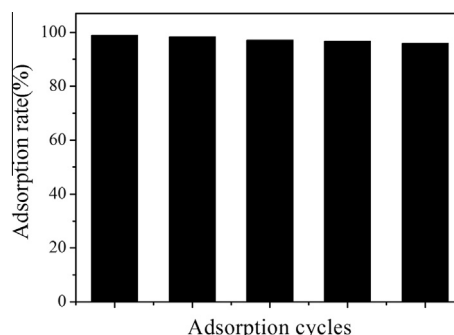


Fig. 8. Regeneration performance of TA-TiO₂.

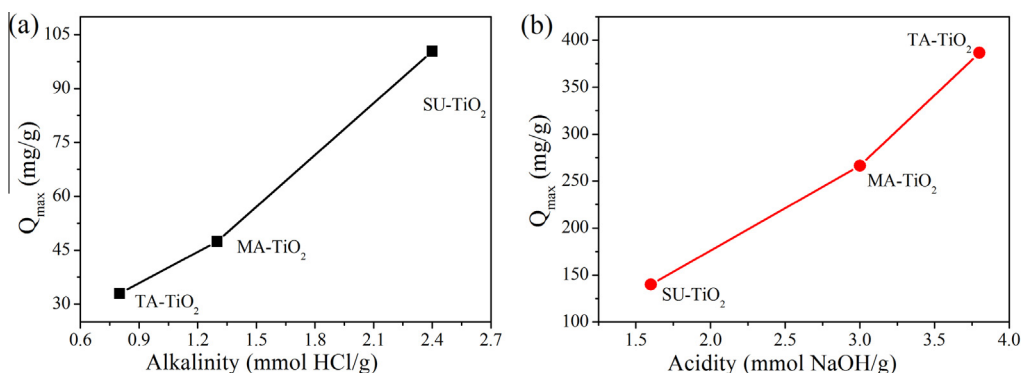


Fig. 9. Correlation between sample acidity/alkalinity and the maximum adsorption amount for ARG (a) and MB (b).

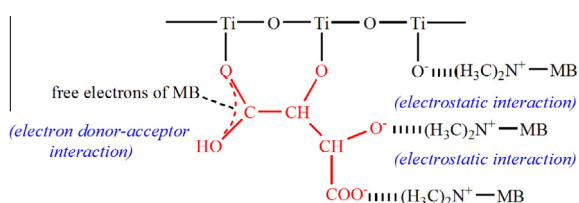


Fig. 10. Proposed adsorption mechanism of MB on TA-TiO₂.

There was a strong correlation between the acidity/alkalinity of TiO₂ and its adsorption capacity, as shown in Fig. 9. It is noted that the TiO₂ adsorbent has a higher adsorption capacity for ARG when its surface shows stronger alkalinity, while it possesses a larger adsorption capacity for MB when it has a stronger acidic surface. TA-TiO₂ with the highest acidity shows the highest adsorption ability for MB, while SU-TiO₂ with the highest alkalinity exhibits the largest adsorption capacity for ARG. Besides, TA-TiO₂ and MA-TiO₂ contain more hydroxyl and carboxyl groups than that of SU-TiO₂ from the TG analyses, especially TA-TiO₂. These groups can facilitate the adsorption of MB (cationic dye) due to the electrostatic attraction. However, the carboxyl groups can impede the adsorption of ARG owing to the electrostatic repulsion. Thereby, the chemical properties (acidity/alkalinity and chemical groups) of TiO₂ play an important role in its adsorption performance.

3.4. Adsorption mechanism

The FT-IR spectra of TA-TiO₂ before and after adsorption were also observed (Fig. S5). The characteristic peaks of carboxyl groups, the antisymmetric and symmetric stretching absorptions of the carboxylate groups disappear after dye adsorption. This suggests that the carboxyl and carboxylate groups take part in the adsorption process. Besides, the band of hydroxyl group in the spectrum of TA-TiO₂ after MB adsorption is shifted from 1626 to 1615 cm⁻¹. This indicates that the hydroxyl groups also involve in MB adsorption. The wide band in the range of 1000–400 cm⁻¹ has an obvious change after MB adsorption, which implies that MB molecule is adsorbed on TA-TiO₂ (Fig. S5a). While the FT-IR spectrum of ARG adsorbed onto TA-TiO₂ has the similar changes (Fig. S5b). So the MB adsorbed on TA-TiO₂ is employed to discuss the adsorption mechanism of the chosen dyes on the as-prepared TiO₂ samples.

According to the above analyses, TA-TiO₂ can adsorb MB through carboxyl and hydroxyl groups via electrostatic attraction. Besides, the results of pH analyses show that TA-TiO₂ still adsorbs MB when the pH value is lower than 3, although the electrostatic repulsion exists between TA-TiO₂ and MB. This suggests that the other interaction involves in the adsorption of MB onto TA-TiO₂.

The carbonyl groups on the surface of TA-TiO₂ can be as the active sites to adsorb MB through the electron acceptor–donor interaction. The proposed adsorption mechanism of MB on the surface of TA-TiO₂ is shown in Fig. 10.

4. Conclusion

The effect of the surface chemical properties of the as-prepared TiO₂ on its adsorption for organic dyes and the adsorption mechanism of the TiO₂ with different amount of hydroxyl- and carboxyl-groups are investigated in this paper. The acidity of the as-prepared TiO₂ is proportional to the number of alcohol group of the used acids, while the basicity of the prepared TiO₂ is inversely proportional to that. The surface of SU-TiO₂ prepared in acid without alcohol group contains a few carbonyl and hydroxyl groups, leading to a basic surface. While the surface of MA-TiO₂ and TA-TiO₂ prepared in acid with alcohol group possesses many carboxyl and hydroxyl groups, resulting in acidic surface. For the adsorption of the anionic dye ARG, SU-TiO₂ displays the largest adsorption capacity due to its strongest basicity. While for the cationic dye MB, TA-TiO₂ has the highest adsorption capacity in virtue of its strongest acidity. Therefore, we deduce that the surface chemical property plays an important role in the adsorption process of TiO₂. The main adsorption mechanism is the electrostatic interaction and the electron acceptor–donor interaction. In summary, the used carboxylic acids can affect the surface chemical properties of TiO₂ samples, and further impact their adsorption capacities.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2015.01.109>.

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