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Effect of hydroxyl group of carboxylic acids on the adsorption of Acid Red G and Methylene Blue on TiO_2

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HIGHLIGHTS

- The surface chemical properties of TiO_2 was proportional to the used acids.
- The surface chemical properties impact the adsorption behaviors of TiO_2 on dyes.
- TiO_2 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 TiO_2 and their adsorption.

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ABSTRACT

While TiO_2 has generated great interest in the removal of organic pollutants in recent years, the effect of the surface chemical property of TiO_2 on the adsorption performance is unclear. Here, TiO_2 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-TiO_2, MA-TiO_2 and TA-TiO_2, 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 TiO_2. Therefore, SU-TiO_2 displayed the largest adsorption capacity for ARG, while TA-TiO_2 had the highest adsorption capacity for MB. Furthermore, TA-TiO_2 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.

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 (HNO_3 or H_2O_2) generates a large amount of acidic surface groups, e.g. carboxyl, anhydride, lactone and phenol groups. The NH_3 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 TiO_2 for its low cost, simple preparation, good stability and non-toxic nature [6–11]. Belessi et al. [7] claimed that the TiO_2 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 TiO_2 for Direct Green 99 was enhanced to 96.77 mg/g, which was more than that of the unmodified TiO_2. Vu et al. [12] suggested that the adsorption capacity of Cu(II) on anatase mesoporous TiO_2 nano-fibers prepared via electrospinning was about 12.8 mg/g.

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Besides, a little attention was paid to the effect of TiO_2 chemical property on its adsorption ability. Li et al. [13] pointed out that the isoelectric point of TiO_2 treated with HCl solution was larger than that of TiO_2 without treatment, which further affected the removal efficiency for oleic acid and oleylamine of the treated TiO_2 and un-treatment TiO_2. Wang et al. [14] indicated that the surface charge of TiO_2 was changed by modified with Nafion, and the Nafion-coated TiO_2 exhibited different adsorption capacity for Reactive Red 22 and Basic Red 2 from the original TiO_2. However, the further study on the influence mechanism of the surface chemical property to the adsorption performance of TiO_2 is favor to its application in the removal of pollutants in water.

Reports indicate that TiO_2 prepared in carboxylic acids can possess different crystal structure [15–17]. However, the effect of the surface chemical property of TiO_2 on the photocatalytic or adsorption performance was not investigated in detail. Herein, we prepared the TiO_2 particles in diverse carboxylic acid systems with different numbers of hydroxyl group. Then, the differences of the surface chemical property in TiO_2 prepared within the selected carboxylic acids were investigated. Furthermore, the effect of the as-prepared TiO_2 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. $FeCl_3 \cdot 6H_2O$, 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 Superpure Water System (EPED, China).

2.2. Synthesis of different acid modified TiO_2

TiO_2 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 TiO_2 samples were named as SU-TiO_2, MA-TiO_2 and TA-TiO_2 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 TiO_2 samples were conducted by the KBr pellet method on BRUKER TENSOR 37 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 N_2 flow at a heating rate of 10 °C/min.

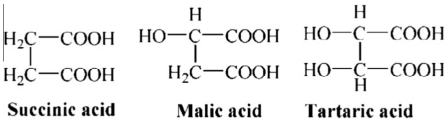

Fig. 2. Molecular structures of succinic, malic and tartaric acids.

Zeta potentials were tested with Malvern Zetasizer Nano ZS90. Samples for zeta potential measurement were prepared by adding 5 mg of TiO_2 in 10 mL NaCl solution (10^{-3} mol/L) at different pH values from 2 to 12 (adjusted with diluted HNO_3 or NaOH solution).

The acidity of the samples was estimated by mixing 0.05 g of TiO_2 with 25 mL NaOH (0.05 mol/L) in a closed flask, and shaked 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 TiO_2 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 TiO_2. 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 TiO_2 Q_t (mg/g) in a certain time t were calculated from Eqs. (1) and (2), respectively:

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

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

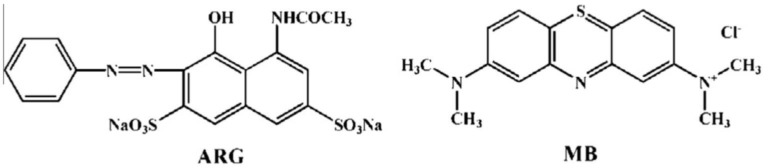

Fig. 1. Molecular structures of ARG and MB.