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Synthesis of PPy-modified TiO_2 composite in H_2SO_4 solution and its novel adsorption characteristics for organic dyes

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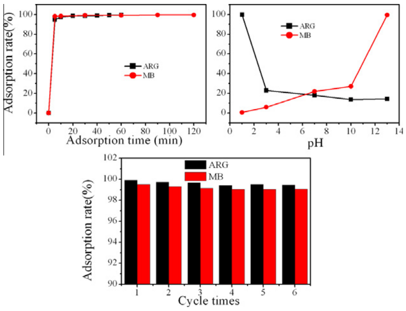
HIGHLIGHTS

- The novel PPy/TiO_2 composite has a potential to treat dye wastewater.
- The H_2SO_4 concentration affects the adsorption ability of the composites.
- The selective adsorption by PPy/TiO_2 can be complete by changing its surface charge.
- The equilibrium adsorption is achieved in a short time of 30 min.
- The composite adsorbent can be reused repeatedly with a high adsorption capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

The PPy/TiO_2 and PPy/P25 composites prepared via the in situ polymerization in H_2SO_4 solution with different concentrations were studied for Acid Red G (ARG) or Methylene Blue (MB) adsorption. Their physicochemical properties were examined by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and zeta potential analysis. The results showed that the H_2SO_4 concentration and the property of metal oxide (self-prepared TiO_2 or commercial P25) obviously affected the nature and adsorption abilities of the PPy/TiO_2 and PPy/P25 composites. The composites can adsorb Acid Red G (ARG) or Methylene Blue (MB) rapidly and reach the equilibrium in 30 min. The adsorption amount of ARG on the composites decreased with the increase of pH value, while the MB removal efficiency increased with pH increase. The adsorption behaviors of ARG and MB on the composites were described by the pseudo-second-order and Langmuir isotherm models. According to the Langmuir isotherm, the PPy/TiO_2 composites exhibited larger maximum adsorption amount than PPy/P25, especially with the PPy/TiO_2 composite prepared in 0.16 mol/L H_2SO_4 (0.16 M-PPy/TiO_2), on which the maximum adsorption amounts of ARG and MB were 218.82 and 323.62 mg/g, respectively. Regeneration experiments revealed that the 0.16 M-PPy/TiO_2 composite can be regenerated easily and reused for six times without visible loss of its original capacity. Additionally, its adsorption efficiencies of ARG and MB in real effluents were still higher than 87% after adsorption–desorption for four times. Through comparing the FT-IR spectra of PPy/TiO_2 before and after adsorption, as well as the surface charge measurement, it can be speculated that electrostatic interaction, hydrogen bonding and specific chemical interaction may be the possible mechanism for the adsorption of ARG and MB by the PPy/TiO_2 composites.

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1. Introduction

Recently, many studies have focused on using TiO_2 as adsorbent, mainly because of its low cost, simple preparation, good stability and non-toxic nature [1–4]. Besides, the hydroxyl groups which present on the surface of TiO_2 can interact with the pollutant molecules, thereby realizing the adsorption of the pollutants [2]. However, the adsorption capacity of TiO_2 was not high compared with that of activated carbon [5–8]. What is more, the studies on the regeneration of TiO_2 are extremely rare, probably due to its low regeneration efficiency [2]. Therefore, the improvement in the adsorption and regeneration capacities of TiO_2 through modification with other materials is highly desired. Some publications have reported that the modified TiO_2 showed better adsorption capacity than the pristine TiO_2 [1,4]. Janus et al. [1] compared the adsorption capacities of unmodified and carbon modified TiO_2, and found the adsorption ability of TiO_2 was improved at least 10 times by modification.

Polypyrrole (PPy) has been used as a modifier for TiO_2 in many studies because of its high thermal stability and non-toxicity [9]. In fact, it is recognized that PPy also has the adsorption ability through ion exchange or electrostatic interaction, largely owing to the existence of positively charged nitrogen atoms in PPy matrix [10–13]. Moreover, PPy can undergo protonation or deprotonation processes when it is immersed in acid or alkali solution, respectively, which results in the change of its surface charges, followed by doping or dedoping of counter ions [14,15]. The capability of reversible transformation of PPy makes it possible that the ions could be adsorbed on or desorbed from PPy, hence, we speculate that it would have an excellent adsorption–desorption property. In this regard, PPy can be considered as a potential modifier to improve the adsorption and regeneration capacities of TiO_2.

Besides, the nature of the prepared TiO_2 and PPy would be affected by the solution pH, and then their adsorption performance would be impacted as well. Dunphy-Guzman et al. [16] investigated the aggregation behavior of TiO_2 particles with different polymorphs as the function of pH, and indicated that the pH value affected the surface adsorption and reactivity of TiO_2 particles. In addition, the crystal structure of TiO_2 was also affected by pH. Tang et al. [17] pointed out that the crystal form of TiO_2 was changed from amorphous to anatase, and then to rutile with the decrease of pH value. Some publications have reported that the adsorption capacity of adsorbent would change with its crystal form [18,19]. On the other hand, PPy can undergo molecular structure or composition changes at the solid/solution interface under different solution pH conditions, making PPy display various surface electric properties, followed by affecting its adsorption performance [15]. In this work, we synthesized a series of PPy-modified TiO_2 (PPy/TiO_2) composite adsorbents in H_2SO_4 solution with various concentrations. Their physicochemical properties were characterized. Also, their adsorption and regeneration properties for Acid Red G (ARG) and Methylene Blue (MB) were studied. The results indicated that the adsorption properties of the composites were affected by H_2SO_4 concentration. Moreover, the composites have different adsorption capacities for anionic and cationic dyes by preprocessing them in solutions with different pH values. This suggested that the PPy/TiO_2 composites may have a potential in selectively adsorbing dyes.

2. Experimental

2.1. Materials

Pyrrole (98%, Qingquan Pharmaceutical & Chemical Ltd., Zhejiang, China) was distilled twice under reduced pressure, and then refrigerated and stored in the dark under nitrogen. P25 power (Evonik Degussa) was obtained from Guangzhou HuaLiSen Trade Co., China. Acid Red G (ARG, 509.43 g/mol) was commercial grade and purified before used. Methylene Blue (MB, 319.86 g/mol) was purchased from Beijing Chemical Reagent Co., China. The structures are shown in Fig. S1. $FeCl_3 \cdot 6H_2O$, HNO_3 (65–68%), H_2SO_4 (98%), CH_3COOH, NaOH, Na_2SO_4, n-propanol (99.9%), sodium dodecyl benzene sulfonate (SDBS), cetyl trimethyl ammonium bromide (CTAB), anhydrous ethanol and tetrabutyl titanate (TBOT, 98%) were of analytical reagent grades and used without further purification. The real effluent used in our study was derived from the printing and dyeing factory in Xi'an. The deionized water used for all the experiments was obtained by an EPED-40TF Superpure Water System (EPED, China).

2.2. Synthesis of adsorbents

The PPy/TiO_2 composites were synthesized by the chemical oxidative polymerization of pyrrole monomer in the pre-prepared TiO_2 suspension solutions with different H_2SO_4 concentrations. The detailed process was described as follows. First, a mixture of TBOT and n-propanol (the volume ratio is 5:2) was added into 200 mL H_2SO_4 solution with different concentrations (0.08, 0.16 and 0.24 mol/L), with magnetic stirring for 24 h. Then the formed suspension solution was cooled to 5 °C, followed by adding 0.675 mL of pyrrole monomer with stirring for 30 min. 25 mL $FeCl_3$ (1.0 mol/L) solution was added dropwise to this mixture, and then the mixed solution was stirred for another 24 h. Finally, the PPy/TiO_2 composites were filtrated and washed with deionized water. The prepared composites, named as 0.08 M-PPy/TiO_2, 0.16 M-PPy/TiO_2 and 0.24 M-PPy/TiO_2 according to the concentration of H_2SO_4, were dried at 50 °C for 24 h.

For comparison, the PPy/P25 composite was also synthesized with the same procedure, except that P25 (2.34 g) was employed instead of self-prepared TiO_2.

2.3. Characterization

X-ray diffraction pattern was obtained with an X'Pert PRO MRD Diffractometer using Cu Kα radiation. Fourier transform infrared spectra (FT-IR) of samples were measured by the KBr pellet method on a BRUKER TENSOR 37 FT-IR spectrophotometer in the range of 4000–400 cm^{-1}. The thermogravimetric (TG) analyses were performed on Setaram Labsys Evo in N_2 flow and at a heating rate of 10 °C/min. The sample morphology was characterized by scanning electron microscopy (SEM, JSM-6700F, Japan). Zeta potentials of samples were measured with Malvern Zetasizer Nano ZS90. It was prepared by adding 5 mg of sample in a 10 mL NaCl solution (10^{-3} mol/L) at different pH values (adjusted with diluted HNO_3 or NaOH solution). The 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).

2.4. Adsorption experiments

All adsorption experiments were carried out in the dark condition at ambient temperature. The suspension containing 300 mg/L of ARG or MB solution and 2 g/L of adsorbent was stirred for 60–120 min. Then the suspension was centrifuged at 4000 rpm for 5 min. The supernatant was analyzed by the UV–Vis spectrophotometer (Agilent 8453). The absorbance values of MB and ARG were read at the wavelength of 665 and 503 nm, respectively.

In order to study the influence of the adsorbent surface potential on the adsorption capacities, the adsorbents were pretreated by HNO_3 or NaOH solutions (pH = 1.0–13.0). Then the treated adsorbents were used to adsorb the same concentration of ARG or MB