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Excellent adsorption and desorption characteristics of polypyrrole/TiO_2 composite for Methylene Blue

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ABSTRACT

P25 or self-prepared TiO_2 coated polypyrrole (PPy/P25 or PPy/TiO_2) composites as novel adsorbents were prepared. Their adsorption–desorption characteristics for Methylene Blue (MB) were comparatively investigated. X-ray photoelectron spectroscopy (XPS) showed that PPy/TiO_2 possessed higher doping level than PPy/P25. Thermogravimetric analysis (TGA) indicated that PPy/TiO_2 contained more PPy than PPy/P25. The results of *water vapor adsorption* suggested that the PPy/TiO_2 composite was more hydrophobic than PPy/P25. The adsorption results revealed that the composites pretreated in the solution with higher pH value exhibited larger adsorption capacities. The ionic concentration in MB solution slightly impacted the removal of MB by the PPy/TiO_2 composite. The adsorption equilibrium results showed that the adsorption of MB was completed in a short time of 30 min. Pseudo-second-order and Langmuir isotherm models were effectively employed to describe the adsorption behavior of MB. PPy/TiO_2 and PPy/P25 were found to have better removal ability for MB compared with pure PPy; especially PPy/TiO_2, on which the maximum adsorption amount was about 3.6 or 5.5 times higher than that of PPy/P25 or pure PPy, respectively. The thermodynamic analysis indicated that the adsorption of MB was spontaneous and endothermic in nature. The regeneration experiments exhibited that PPy/TiO_2 can be reused at least seven times without obvious loss of its original adsorption capacity. Electrostatic interaction, hydrogen bonding and hydrophobic interaction played the roles in MB adsorption performance. It is expected that the PPy/TiO_2 composite can be considered as a stable adsorbent for dye removal.

1. Introduction

The generated dye effluents from dye industries can cause serious water pollution problems if directly discharged into the environment. Therefore, it is important to remove dyes from dye wastewater. Recently, various treatment processes have been widely employed to remove dyes from wastewater [1]. In these methods, adsorption has been proved to be a reliable treatment approach due to its low capital investment, abundant raw material source, simple in design and operation, and non-toxic [2,3]. However, the choice of appropriate adsorbent for real applications is still a challenging issue. Although activated carbon is the present research focus, it also has many shortcomings, such as relative high cost of investment and operating, regeneration difficulty, and long time to adsorption equilibrium [4,5]. Therefore, the development of new adsorbents with excellent adsorption and regeneration capacities becomes the research focus.

Polypyrrole (PPy) is one of the most commonly investigated conducting polymers owing to its non-toxic nature, environmental stability, low cost and simple preparation [6]. Because of the existed positively charged nitrogen atoms in PPy matrix, PPy possessed the adsorption ability through ion exchange or electrostatic interaction [6–8]. Moreover, PPy can undergo protonation or deprotonation processes when it is treated with acid or alkali solution, resulting in the change of its surface charges, followed by the doping or dedoping of counter ions [9,10]. Owing to the reversible transformation capability, PPy would have excellent regeneration ability, but this was rarely reported. Nevertheless, pure PPy showed a poor adsorption capacity [8,11]. Some publications have reported that the composites formed through PPy polymerizing on the surface of substrate materials can provide improved adsorption capacity, as compared with pure PPy [12,13]. Baumik et al. [12] prepared the PPy/Fe_3O_4 magnetic composite and found that its maximum adsorption capacity for Cr(VI) could reach 169.4 mg/g at 25 °C. Lim et al. [13] fabricated PPy/silica nano-composite and testified that it could selectively adsorb Hg^{2+} with the amount of 0.97 mmol/g.

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However, the publications on the effect for the property of the selected substrate material on the adsorption capacity of composite were rarely reported. In this study, two kinds of titanium dioxide, the self-prepared TiO_2 (without calcination) and commercial P25, were chose as the substrate materials to synthesize the corresponding composite sorbents (PPy/TiO_2 or PPy/P25). Then their physicochemical properties and adsorption–desorption performances for Methylene Blue (MB, cationic dye) were studied. Pure PPy was also tested for comparison. In normal sol–gel processing, TiO_2 particles without calcination did not have complete crystallization and showed mainly amorphous. Zhang et al. [14] and Hoang et al. [15] indicated that the surface Ti atoms of the amorphous TiO_2 could not have full coordination, which existed in the forms of TiO_5 and TiO_4. This resulted in more structure defects in the amorphous TiO_2. Then the uncoordinated Ti atoms can act as active sites for chemical binding through ester-like linkage, bridging and chelating [14]. While P25 possessed complete and perfect crystallization, so its defects were relatively low. Therefore, the different nature of the amorphous TiO_2 and P25 may bring about the difference in the adsorption performance of the prepared PPy/TiO_2 and PPy/P25. The adsorption results exhibited that the PPy/TiO_2 and PPy/P25 composites possessed higher removal efficiencies than pure PPy. Moreover, the PPy/TiO_2 and PPy/P25 composites had different adsorption ability though they had a similar specific surface, and the adsorption amount of PPy/TiO_2 was nearly 3.6 times higher than that of PPy/P25. This suggested that the property of the selected substrate would severely impact the adsorption performance of the prepared composites. Additionally, the regeneration experiments indicated that the composites had the excellent adsorption stability.

2. Experimental

2.1. Materials

P25 powder (P25, Evonik Degussa) was purchased from Guangzhou HuaLiSen Trade Co., China. Pyrrole (98%, Qingquan Pharmaceutical & Chemical, Ltd., Zhejiang, China) was distilled twice under reduced pressure, and then stored in the dark under low temperature. Methylene Blue (MB) was purchased from Beijing Chemical Reagent Co., China. $FeCl_3 \cdot 6H_2O$, CH_3COOH, HNO_3 (65–68%), NaOH, n-propanol (99.9%) and tetrabutyl titanate (TBOT, 98%) were of analytical grade and used without further purification. The deionized water used for all experiments was obtained from the EPED-40TF Superpure Water System (EPED, China).

2.2. Synthesis of adsorbents

The preparation process of PPy/TiO_2 was described as follows. First, a mixture of TBOT and n-propanol with the volume ratio of 2.5:1 was added into 0.16 mol/L of HNO_3 solution (65 °C, 400 mL) with magnetic stirring for 2 h. A translucent TiO_2 solution was formed, followed by cooling down to ambient temperature. Then the TiO_2 solution was transferred to a 500 mL flask and cooled to 5 °C with mechanical stirring. Afterwards, pyrrole (0.25 mL) was added to the solution and stirred for 30 min, followed by adding dropwise $FeCl_3$ (1 mol/L, 10 mL) solution in 1 h. Then the mixture was reacted for additional 24 h statically. Finally the generated black solid was filtered and washed with deionized water several times, and then dried at 50 °C for 24 h. The solid was the PPy/TiO_2 composite.

For comparison, PPy/P25 was synthesized in the same recipe, except that the TiO_2 solution was replaced with P25 suspension (0.117 g/L). Pure PPy was synthesized in the same synthesis conditions except no P25 adding.

2.3. Characterization

X-ray diffraction (XRD) patterns were obtained with X'Pert PRO MRD diffractometer using Cu Kα radiation. Raman spectra were recorded using Horiba HR800 Raman spectrophotometer. 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). The oxidative states of the samples were determined using X-ray photoelectron spectroscopy (XPS) on Kratos Axis Ultra DLD with an Al monochromatic X-ray source (1486.71 eV). All binding energies (BEs) were referenced to the C1s hydrocarbon peak at 284.6 eV. The thermogravimetric (TG) analyses were performed on Setaram Labsys Evo in N_2 flow and at a heating rate of 10 °C/min. The morphologies were characterized by scanning electron microscopy (SEM, JSM-6700F, Japan). The zeta potentials were measured with Malvern Zetasizer Nano ZS90. Samples for zeta potential measurement were prepared by adding 5 mg of composite in 10 mL NaCl solution (10^{-3} mol/L) at different pH values (adjusted with diluted HNO_3 or NaOH solution).

Water vapor adsorption was regarded as a good means to evaluate the surface hydrophobicity of adsorbent. The adsorbent adsorbing a lower amount of water vapor was known to be more hydrophobic [16,17]. The process was similar to what was used by Wu et al. [17], except that the drying condition was 50 °C for 8 h, and the water vapor adsorption condition was 25 °C for 12 h.

2.4. Adsorption experiments

In order to study the influence of surface charge on the adsorption property, the adsorbents were pretreated with HNO_3 or NaOH solution (pH = 1.0–13.0, 5 mL). Then the pretreated adsorbents were centrifuged and used to conduct the MB solution without any processing (300 mg/L). The effect of ionic concentration (0–0.3 mol/L) on the adsorption was carried out by adding Na_2SO_4 into the 300 mg/L MB solution.

All adsorption experiments were carried out in dark condition at 25 °C. The suspension containing 300 mg/L of MB solution and 2 g/L of adsorbent was stirred for 2 h. Then the suspension was centrifuged at 4000 rpm for 5 min. The supernatant was analyzed by the UV–vis spectrophotometer (Agilent 8453). The absorbance value of MB was read at the wavelength of 665 nm.

The adsorption rate R (%) and the amount of dye molecules adsorbed onto the adsorbents Q_t (mg/g) after the certain time t were calculated from Eqs. (1) and (2), respectively:

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

$$Q_t = \frac{C_0 - C_t}{M} \times V \tag{2}$$

where C_0 is the initial concentration (mg/L), C_t is the residual concentration at time t (mg/L), V is the solution volume (L), and M is the adsorbent mass (g).

The adsorption equilibrium of MB with different concentrations (200, 300 and 500 mg/L) on PPy/TiO_2 was evaluated at 25°C, with 2 g/L of PPy/TiO_2 added and stirred for 2 h. The adsorption kinetics was investigated using the pseudo-first-order and pseudo-second-order models. Their linear forms are described in Eqs. (3) and (4), respectively:

$$\log(Q_{eq} - Q_t) = \log Q_{eq} - \frac{K_1}{2.303} t \tag{3}$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_{eq}^2} + \frac{t}{Q_{eq}} \tag{4}$$