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Enhancement of methyl violet removal by modification of TiO_2 nanoparticles with AgI

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ABSTRACT

Nanostructured AgI/TiO_2 was synthesized by deposition–precipitation method. The AgI/TiO_2 nanoparticles with different size were characterized using XRD and TEM methods. In order to compare the activity of these nanoparticles for removal of environmental pollutants, the adsorption of methyl violet by particles was studied. The equilibrium adsorption data were fitted to the different isotherms. The equilibrium data show that the modification of TiO_2 nanoparticles with AgI, leads to the higher adsorption capacity (more than twice) for methyl violet. The kinetic data for adsorption of methyl violet indicates that modification of TiO_2 with AgI leads to a stable adsorption.

1. Introduction

Dye pollutants from textile paper and other industries are an important source of environmental contamination [1]. Environment and living organs can be affected by the dyes in the effluent of industries, even in low concentration. Usually synthetic dyes cannot be destroyed by light or oxidizers, thus adsorption is one of the best methods for the removal of dyes from waste water [2–4]. Methyl violet (M.V.) which is a basic dye, has harmful effects on living organisms and its inhalation may cause different illnesses such as headaches, diarrhea and etc. [5].

Adsorption as a simple and low cost method can produce high quality water while also being a process that is economically feasible [5]. Some adsorbent for methyl violet removal (as dye pollutants) are cellulose-based wastes [6], Bagsse fly ash [7] cross linked amphoterie starch [2], sepiolite [8,9] mansonia sawdust [5,10] and activated carbon [11].

All these studies confirm that the dye removal is possible by adsorption. Also photocatalytic decomposition is an efficient method for removal of dyes from water [1–8]. Performance of adsorption process is related to the both physical and chemical properties of adsorbate and adsorbent [12].

Nanostructured titanium dioxide (TiO_2) is a semiconductor and its chemical stability is high, thus it was extensively used as a photocatalyst and adsorbent during the past two decades [13–19].

On the other hand adsorption of ionic dyes (methylene blue and blue 40) onto TiO_2 has been investigated, too [15]. Recently, we have investigated the adsorption of methyl violet onto TiO_2 nanoparticles with different phase (including different percentage of Anatas and Rutile phases) from kinetic point of view [16].

Modification of TiO_2 is one of the hot topics in the field of photocatalysis [13]. These works include (1) doping of TiO_2 with different metal atoms such as Pt, Au, Ag, Cr, V, etc., (2) doping of TiO_2 with varies nonmetal atoms including N, C, S, B, I, Br, F, etc. and (3) anchoring an organic dye sensitizer molecule on the surface of the photocatalyst [13]. Recently Hu et al. prepared P25 titania supported AgBr and AgI by deposition–precipitation method [19]. The prepared nanostructured AgI/TiO_2 photocatalyst showed much higher photocatalytic activity for the destruction of crystal violet and 4-chlorophenol under visible light irradiation than pure titania [13]. Briefly, due to modification of TiO_2, there appears to be a decrease in the band gaps along with an increase in yield quantum of chemical reactions. There is also a decrease in the stable intermediates during the photocatalytic reactions [17].

The purpose of the present work is to investigate the ability of AgI/TiO_2 nanoparticles with different sizes, for removal of methyl violet from aqueous solution by adsorption method and compare their ability with pure TiO_2 nanoparticles.

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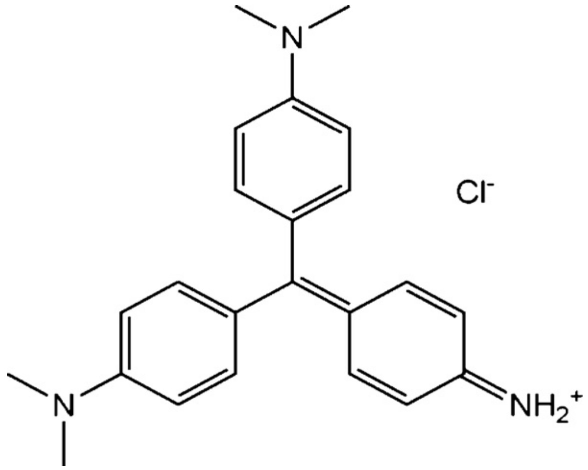

Scheme 1. Chemical structure of methyl violet.

2. Material and methods

2.1. Adsorbate

We used methyl violet manufactured by Merck Co. as an adsorbate while we did not apply any purification. Scheme 1 shows the chemical structure of M.V. [18]. To prepare stock solution, we dissolved accurately weighted quantities of M.V. in distilled water so that we can obtain other desired concentrations of solutions through successive dilutions.

2.2. Adsorbent

Titanium dioxide nanoparticles in powder form and different sizes were used. TiO_2P25 with particle size 20 nm from Deggusa and TiO_2(B) with particle size 70 nm from nano Co. Pars were used as precursor for AgI/TiO_2 nanoparticles preparation. AgI/TiO_2 containing Ag 10 wt% was prepared by the deposition–precipitation method according to the recent report [19]. Briefly 1 g of TiO_2 nanoparticle and 0.205 g of KI were dissolved in 100 ml of distilled water and 1 g of TiO_2 nanoparticle were added to this solution, then 0.21 g of $AgNO_3$ in 2.3 ml of NH_4OH (25 wt% NH_3) was added to the mixture, rapidly. The obtained suspension was stirred by magnetic stirrer at room temperature for 12 h. Then the solution was filtered and the obtained product was washed with water, and dried at 70 °C. The obtained yellow powder is AgI/TiO_2 nanoparticle [13].

2.3. Adsorption studies

All batch adsorption experiments were under dark conditions and at 30 °C. The residual concentration of M.V. has been measured by UV/visible spectrophotometer (PG Instrument T 80) at 585 nm.

For kinetic studies the initial dye concentration and the mass of adsorbent were $3.4 \times 10^{-3}\ \text{g}\ \text{l}^{-1}$ and 0.01 g, respectively. For equilibrium studies a series of 5 ml of M.V. solutions with different initial concentrations (C_0) and a 0.01 g of the adsorbent were contacted with each other in the 10 ml flasks. Then the mixtures were put into an ultrasonic batch to disperse the adsorbent for 6 min. The flasks were placed in a water batch shaker and shaken at 150 rpm for 24 h to ensure the adsorption process reaching equilibrium at dark condition. After that, the suspensions were centrifuged and the equilibrium concentration of M.V. in the bulk (C_e) was determined using UV/visible spectrophotometer. For calculation of the amount of adsorbed dye per unit mass of adsorbents ($\text{mg}\ \text{g}^{-1}$) at any time (q_t) and at equilibrium (q_e) the following equations were used, respectively:

$$q_t = \frac{C_0 - C_t}{m} \times V \tag{1}$$

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{2}$$

where C_0, C_e and C_t are the initial, equilibrium and at any time dye concentration, m_{TiO_2} is the adsorbent mass (g) and V is the solution volume (L).

3. Results

3.1. Characterization of the modified TiO_2

Fig. 1 shows the XRD pattern of synthesized AgI/TiO_2(P25) and AgI/TiO_2(B). The XRD patterns clearly indicates the formation of

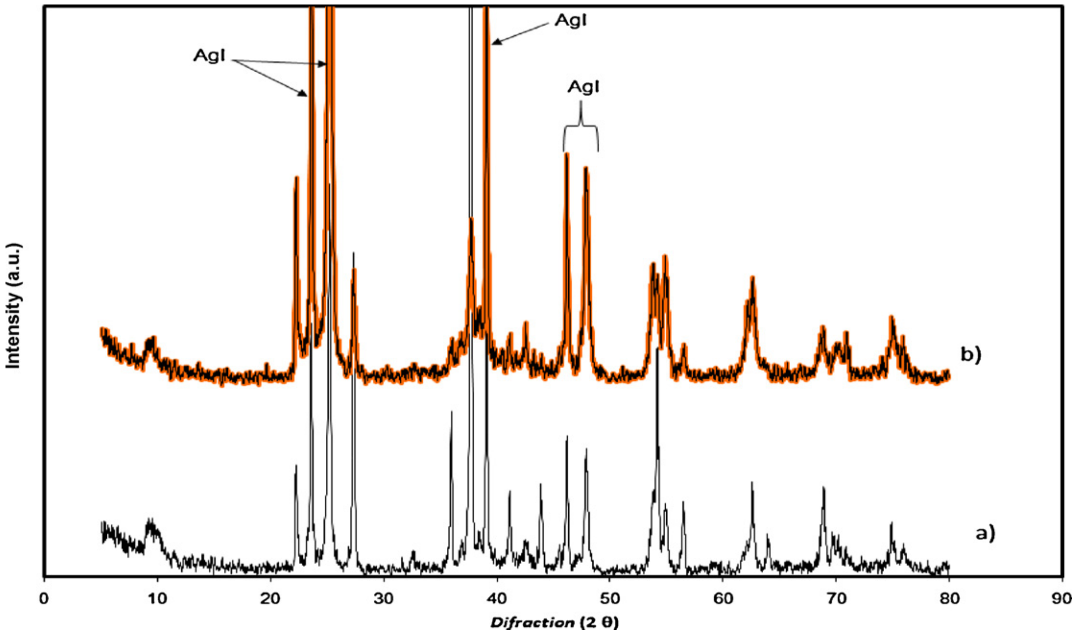

Fig. 1. XRD patterns of modified TiO_2 nanoparticles: (a) AgI/TiO_2(P25); (b) AgI/TiO_2(B).