Journal of Industrial and Engineering Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Carbon and CNT fabricated carbon substrates for TiO_2 nanoparticles immobilization with industrial perspective of continuous photocatalytic elimination of dye molecules

Elmira Pajootan*, Mehdi Rahimdokht, Mokhtar Arami

Textile Engineering Department, Amirkabir University of Technology, 424 Hafez Ave., Tehran 15875-4413, Iran

ARTICLE INFO

Article history:
Received 24 August 2016
Received in revised form 20 June 2017
Accepted 21 June 2017
Available online xxx

Keywords:
TiO_2 nanoparticles
Electrodeposition
Immobilization
Solvent evaporation
Response surface methodology

ABSTRACT

We utilize carbon nanotubes fabricated carbon plates with large surface area and high adsorption capacity as the substrate to immobilize TiO_2 nanoparticles without any agglomeration using solvent evaporation method. The photocatalytic activity is investigated in a continuous photocatalytic reactor to degrade three acid dyes, which is shown to be stable for 16 successive cycles. Response surface methodology (RSM) is used to optimize and model the binary system for a closer simulation of real industrial wastewater with the electrical energy consumption below 0.5 KWh/g_{COD}. A fast and complete decolorization was achieved in 100 min by adding H_2O_2 to the system.

Introduction

Nowadays, nanotechnologies are introduced as a preferable solution to current water and wastewater treatment methods to improve the water quality to meet the environmental standards and to conquer the water scarcity resulted from the human activities in both developing and industrialized countries. Titania nanoparticles (TiO_2) are one of the most studied semiconductors for the degradation of pollutants existing in water streams, and also in many other applications, such as sunscreen, surface coating, solar cells, environmental remediation, etc. due to their semiconducting properties and photostability [1–5].

When TiO_2 is irradiated by UV light, the photoinduced electrons and holes (e^-/h^+) are formed. OH^- and H_2O as electron donors and oxygen as electron acceptor will form the hydroxyl ($OH^\bullet$) and superoxide ion radicals ($O_2^{-\bullet}$). These generated radicals especially hydroxyl radicals are nonselective strong oxidants which can fully mineralize organic pollutants [6,7].

One of the major drawbacks of the usage of TiO_2 nanoparticles (NP) is the problem encountered through their separation and removal from the treated solutions. The UV absorption of these photoactive and nano-sized materials has a potential toxicity to organisms and environment, to which many investigations are dedicated in order to survey the phototoxicity and dramatic effect of TiO_2 NP. Therefore, immobilization of these nanoparticles is now the subject of most enquiries pertaining to the area of this science [1–4,8–10].

In addition, the practical application of slurry TiO_2 solutions can be very challenging in the continuous wastewater treatment processes. Furthermore, the application of TiO_2 NP for photocatalytic processes suffers from a low quantum efficiency because of the rapid recombination of the photoinduced electrons and holes (e^-/h^+), mass transfer and photon transfer limitations [11,12].

Several methods have been developed to enhance the photocatalytic efficiency; in this regard, carbon nanotubes (CNT) with large specific surface area and excellent electrical properties have received tremendous attention for building the composite materials. These nanotubes can also be used as supporting material for TiO_2 NP owing to their nanomorphology, high mechanical and chemical stability and high structural integrity [4,11,13–17]. This combination can significantly improve the photocatalytic performance by lowering the recombination of e^-/h^+ couples, and the combination of their electronic, adsorption, mechanical and thermal properties [18–21].

Various techniques have been reported to coat titania NP on carbon-based supports for different purposes such as: hydrolysis of $TiCl_4$ [22], deposition of TiO_2 by sol-gel method [23], mixing TiO_2 with carbon materials [24], electrodeposition [25], precipitating

* Corresponding author.
E-mail address: pajootan@aut.ac.ir (E. Pajootan).

http://dx.doi.org/10.1016/j.jiec.2017.06.039
1226-086X/

[26,27], hydrothermal treatment [28,29], solvent evaporation [30], etc.

Nowadays, response surface methodology (RSM) is one of the most popular experimental design and optimization tools being used in a wide range of applications especially wastewater treatment. Reducing the number of experiments while maintaining the accuracy of results, response surface modeling through regression, process optimization and prediction of the variables' values, exploration the interactions of various combinations of parameters are some of the advantages of RSM technique [31–33].

In this research, we successfully demonstrated the immobilization of TiO_2 NP on carbon-based material to decolorize the simulated textile wastewater by photocatalytic process in a continuous reactor. For this purpose, the relatively low-cost and available carbon-based materials and TiO_2 NP, with their specific characterizations were taken into consideration. First, CNT were electrodeposited on the surface of the carbon plates via a method reported in our previous study [34]. Then, a solution containing dispersed TiO_2 NP were added to the surface of the carbon plates (TiO_2-C) and CNT fabricated carbon plates (TiO_2-CNT). Finally after the evaporation of the solvent, TiO_2 NP were immobilized on the plates. FESEM images and FTIR spectra indicated the characteristics of the prepared plates. The prepared plates were successfully employed for the continuous decontamination of wastewater with appropriate stability for several cycles. The decolorization and further degradation of the contaminated solutions containing C.I. Acid Red 14, C.I. Acid Blue 92 and C.I. Acid Yellow 117 were investigated and the effect of important parameters including pH, initial dye concentration and TiO_2 dosage was demonstrated. RSM was applied to design the experiments to evaluate the effect of parameters in the degradation of dyes from binary solutions and to multi-optimize the degradation process considering maximum dye and COD removal (%), as well as minimum electrical energy consumption as the responses to develop a cost effective system. The variation of dye removal efficiency by changing the flow rate and addition of hydrogen peroxide was evaluated as well.

Experimental

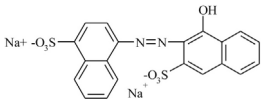
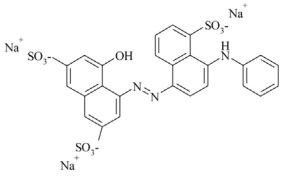
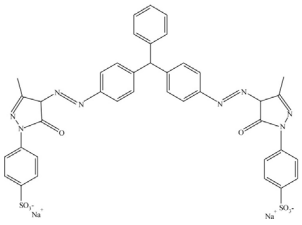
Materials

In all experiments, the reagents were of analytical grade. Titania NP (Degussa P25) was employed as the photocatalyst (average particle size: 30 nm, purity >97% with 80:20 anatase to rutile). Cetyl Trimethyl Ammonium Bromide ($(C_{16}H_{33})N(CH_3)_3Br$, CTAB) and MWCNT (purity >95%, length 10–20 μm and diameter 30–50 nm) were purchased from Merck and Neutrino, respectively. C.I. Acid Red 14 (AR14), C.I. Acid Blue 92 (AB92) and C.I. Acid Yellow 117 (AY117) (Ciba Co.) which are widely used in textile industry, were employed as synthetic dyes (Table 1). H_2SO_4 (1 M) and NaOH (1 M) (Merck) were used to adjust the pH of dye solutions. Carbon substrates (purity >95%) with the dimension of $50 \times 110 \times 3\ mm^3$ used as the supporter for titania naoparticles were purchased from Seraaj Co. The hydrogen peroxide (H_2O_2, 30%) was supplied from Loba Chemie.

Immobilization of TiO_2 NP

The carbonaceous support (Carbon and CNT fabricated carbon substrates) were selected as substrates for the immobilization of TiO_2 NP due to their excellent adsorption properties and chemical inertness, especially CNT. The fabrication of carbon plates using CNT by a novel, facile and inexpensive electrodeposition technique was fully explained in a separate investigation in our previous study [34]. In summary, the carbon plates were abraded with sand paper and washed with distilled water. Then each electrode was pretreated with 50 mL of NaOH (10% w/v), 50 mL of HNO_3 (50%, v/v) and 50 mL of acetone, each step for 5 min, respectively, and then they were rinsed with distilled water for three times. The electrodeposition procedure to form a thin layer of CNT on the surface of carbon plates was performed by applying the DC voltage of 17.5 (V) to a 200-mL solution containing 0.06 g of CNT and 0.04 g of CTAB which had been sonicated for 60 min using Delta D68H

Table 1
Dyes characteristics.

C.I. generic name	λ_{max} (nm)	Molecular weight (g/mol)	Formula	Structure
C.I. Acid Red 14	515	502.42	$C_{20}H_{12}N_2O_7S_2{\cdot}2Na$	
C.I. Acid Blue 92	572	695.58	$C_{26}H_{16}N_3O_{10}S_3{\cdot}3Na$	
C.I. Acid Yellow 117	440	848.83	$C_{39}H_{30}N_8O_8S_2{\cdot}2Na$	

Please cite this article in press as: E. Pajootan, et al., Carbon and CNT fabricated carbon substrates for TiO_2 nanoparticles immobilization with industrial perspective of continuous photocatalytic elimination of dye molecules, J. Ind. Eng. Chem. (2017), http://dx.doi.org/10.1016/j.jiec.2017.06.039