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Performance of COD Removal from Acid Scarlet BS-Containing Solution in a Novel Packed-Bed Hollow-Tube Photocatalytic (PHP) Reactor

Ya Xiong,[1,*] Chun He,[1,2] Taicheng An,[1] Quan Yu,[1] Changhong Zha,[1] and Xihai Zhu[1]

[1]School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou, P.R. China
[2]Department of Chemistry, Zhaoqing College, Zhaoqing, P.R. China

ABSTRACT

A novel packed-bed hollow-tube photocatalytic (PHP) reactor using TiO_2-coated Ti particles as fillers was designed and applied to treat a simulated dye wastewater containing Acid Scarlet BS. The experimental results showed that PHP reactor could efficiently remove chemical oxygen demand (COD) from the dye solution and the COD removal efficiency was considerably dependent on the operating parameters, airflow, initial dye concentration and initial pH value of solution. It was also found that the inserting of the hollow tubes could apparently increase the COD removal efficiency of the packed-bed photo-reactor while the application of external electric field could improve the degradation efficiency of the dye but not obviously promote COD removal.

*Correspondence: Ya Xiong, School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou, 510275, P.R. China; Fax: 0086-02-8411363; E-mail: cesxya@zsu.edu.cn.

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INTRODUCTION

TiO_2-mediated photocatalytic degradation of organic pollutants has become a growing area of environmental researches.[1–4] The appeal of this process technology is the prospect of complete mineralization of the organic pollutants into harmless compounds.[5] To date photocatalytic processes are generally conducted in two kinds of reactors: (a) slurry-photocatalytic reactor, (b) immobilized-film photocatalytic reactor. For the former, TiO_2 photocatalyst is employed in a suspension of submicrometer semiconductor material, and therefore an additional separation step is required to remove the catalyst from large volume of water. This presents a major drawback for the application of slurry-photocatalytic reactor to treating wastewater. For the latter, there is no need for additional equipment and energy for the recovery of catalyst particles and it seems to be preferable for technical application. However, this kind of reactor has only a thin coating on a surface. Thus, the amount of active catalyst in the reactor is limited, compared to slurry-photocatalytic reactor and a decrease of photocatalytic degradation efficiency by at least a factor of 10 was reported.[6] This problem severely restricts its processing capacity. To minimize the problem, concerning researches have been carried out by the application of packed-bed photocatlytic reactor because this kind of reactor has a greater ratio of volume-surface and provides large amount of active catalyst. However packed-bed photocatalytic reactor has a unique problem that the distribution of light is not considerable uniform. To overcome the inherent deficiencies in the packed-bed photocatalytic reactor, we will introduce hollow quartz glass tubes in the reactor. We believe that this distributive type of photocatalytic reactor will allow UV light to better passage through the packed-bed and has a larger illuminated area.

The other hurdle in the practical application of TiO_2 photocatalytic process is lower photocatalytic efficiency mainly due to the high degree of combination of photogenerated electron and hole. Several attempts have been performed to suppress this combination such as the application of anodic bias,[7] noble metal deposition[8] and metal loading.[9]

In the present paper, TiO_2 photocatalysts were immobilized on chemically stable metal Ti particles. Expectedly, these Ti particles will act not only as support, like quart sand, fly ash, hollow glass spheres, polyethylene sheets, and glass etc., but also as sinks for the photogenerated electrons, similar to metal-loading, that is, the excited electrons immediately transfer to Ti site, avoiding rapid recombination of hole and electron. Our project will devote to developing a novel packed-bed hollow-tube photocatalytic (PHP) reactor using these TiO_2-coated Ti particles as packed material. As a primary work, the present investigation is mainly focused on the performance of COD removal from the simulated wastewater containing Acid Scarlet BS (Fig. 1) in the PHP reactor.

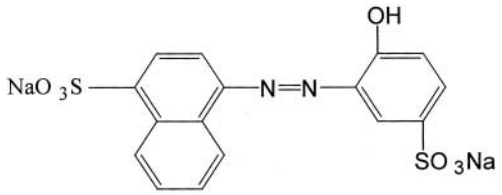

Figure 1. Chemical structure of Acid Scarlet BS.

EXPERIMENTAL

Materials

The used photocatalyst was titanium dioxide (Degussa P25) with a surface area of $50\,m^2\,g^{-1}$. Ti particles have a purity of 99.9% and a size range of 20–40 mesh. Acid Scarlet BS was a commercial azo dye, and the solution was prepared with deionized water to $0.4524\,g\,L^{-1}$ (COD: 153 ppm) and no pH value was adjusted except indicated.

Preparation of TiO_2-coated Ti Particles

In a typical coating procedure, 300 g Ti particles were cleaned with ethanol in an ultrasonic bath for 30 min, and then washed three times using deionized water. A 0.3-L aqueous suspension of TiO_2 ($50\,g\,L^{-1}$) was agitated and sinicated for 30 min before coating. The titania suspension was mixed with these cleaned Ti particles and then mechanically agitated for 2 h. The coated Ti particles were separated from the resulting mixtures by filtration and then dried on a hot plate at 100°C and finally sintered 2 h in an oven at 400°C. Coating, drying and sintering was repeated two times. Scan Electron Microscopy (SEM) observation showed a dense coverage of Ti with TiO_2 particles (0.08) W/W (TiO_2/Ti).

Apparatus and Analysis

A UV-PC3101PC spectrophotometer (SHIMASZU, Japan) was used for recording the UV absorption spectra of solution. Scanning electron microscope (SEM) images were obtained on a JSM-6330F-mode Field Emission Scanning Electron Microscope (JEOL, Japan), X-ray diffraction (XRD) was performed on X-ray reflection diffraction (XRD) was performed using D/Max-IIIA Diffratometer (Rigaku Corporation, Japan) with Radiation of Cu target ($K \propto 1, \lambda = 1.54056\,nm$). The determination of Energy Dispersive X-ray Spectrometer (EDS) was conducted using D/Max-IIIA Diffratometer (Rigaku Corporation, Japan) and S-520 SEM link ISIS-300 Energy Dispersive X-ray Spectrometer. Chemical oxygen demand (COD) was measured with potassium dichromate after the sample was digested with a

WMX COD microwave digestion system.[10] It reflects the amount of organic pollutants in the sample.

Photocatalytic Set-up

The schematic drawing of the PHP reactor is presented in Fig. 2. The apparatus consists of four parts: a 500 W high-pressure mercury lamp with a reflector; a double-welled cooling quartz glass tube with a 5.0 mm-thick cooling water; a batch glass reactor ($7 \times 3 \times 3$ cm) with 60 hollow tubes (inside diameter: 2.8 mm) and 50 g TiO_2-coated Ti particles; and compressed-air. The UV lamp was placed in the cooling quartz tube with a cooling water flow (650 mL min^{-1}) to maintain reaction isothermality. The circulating water also ensured infrared filtering of the incident ray. The UV lamp was located 8 cm above the surface of the packed TiO_2-coated Ti particles in the reactor. In photoelectrocatalytic experiments the PHP set-up was reformed to an undivided photoelectrocatalytic reactor by adding two Ti plate electrodes (2.8×2.8 cm) and DC Power supply, as shown in Fig. 2.

Photocatalytic Set-up Experimental Procedure

Prior to starting photocatalytic reaction, a 25.0 mL simulated wastewater was fed into the photoreactor. The reactor was timed starting as illumination and compressed air supply were switched on. Except as indicated, general treating conditions were 0.06 $m^3 h^{-1}$ airflow and 60 min for a batch run. The resulting solution was remained for optical absorption and COD analysis. Photoelectrolysis: Except for

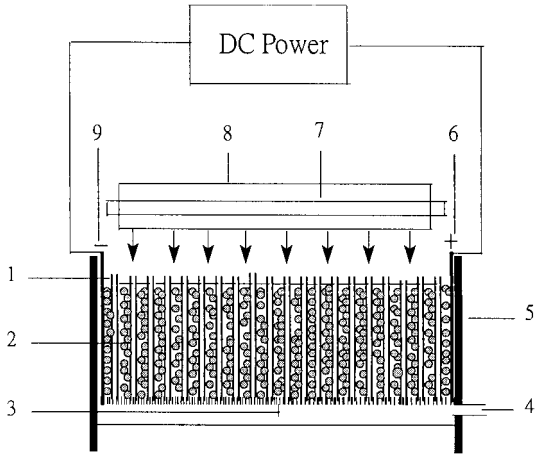

Figure 2. Schematic drawing of HPP reactor (1, Quartz glass hollow tube; 2, TiO_2-coated Ti particles; 3, micropore plate; 4, inlet of compressed-air; 5, support; 6, anode; 7, UV light; 8, double-welled quartz glass cooling tube with a 5.0 mm-thick cooling water; 9, cathode).

that a 30-V cell voltage was applied to PHP reactor during experiment, other procedures were identical to that of photocatalytic process.

RESULTS AND DISCUSSION

Surface Characterization of TiO_2-coated Ti Particles

The resulting Ti particles were completely covered by TiO_2 coating layer. The SEM image of the coating was shown in Fig. 3. It can be seen from the Fig. 3 that these immobilized TiO_2 particles on Ti particles has a diameter range of about 50–100 nm, greater than that of original P25 TiO_2. This observation implies that the colloidal TiO_2 particles are aggregated in the process of immobilization. However, XRD analysis (Fig. 4) shows that these immobilized TiO_2 exist in two kinds of forms, anatase and rutile phases, and EDS determination further confirmes that the ratio of anatase and rutile is proximately 7 : 3, similar to P25 TiO_2.

Comparison of Two Packed-Bed Photocatalytic Reactors With and Without Hollow Tubes

Unlike other reported TiO_2 fixed-bed reactors, which typically have a thin film of wastewater passing over a large open surface, the PHP reactor has a packed-bed configuration with a 3-cm bed-depth (Fig. 2). The penetration or distribution of light, one major barrier for packed-bed photocatalyic reactor, can be expectedly improved by evenly inserting hollow quartz tubes. Experimental results shows that PHP reactor can remove 86.7% COD from simulated wastewater containing Acid Scarlet BS in 60 min while packed-bed photoreactor without the hollow tubes only could remove 76.1% COD from the same solution. The inserting of 60 hollow tubes

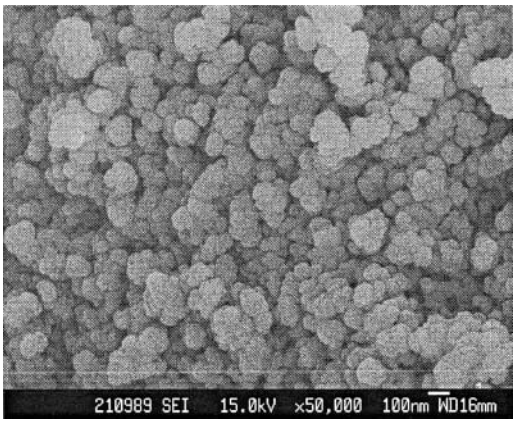

Figure 3. SEM image of TiO_2-coated Ti particles.

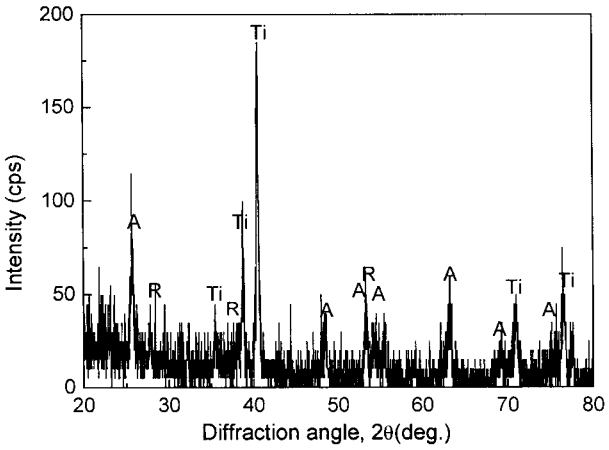

Figure 4. XRD pattern of TiO_2-coated Ti particles.

could increase about 10% COD removal efficiency. The following investigations will devote to probing the effect of operating parameters on the COD removal efficiencies of PHP reactor.

Effect of Airflow

It is well known that oxygen is essential to increase photocatalytic efficiency of slurry or thin film photocatalytic reactor without external anodic bias due to its ability of scavenging photogenerated electrons and suppressing the recombination of the electrons and holes.[11–13] In the present work, air, instead of pure oxygen, was purged into the solution from the reaction bottom. It was observed that air played an important role in the photocatalytic degradation of Acid Scarlet BS for PHP reactor, similar to pure oxygen. Figure 5 presents the dependence of the COD removal efficiency on airflow.

In the absence of air, total COD removal efficiency is 53.4%. If the contribution of packed-bed adsorption to COD removal, 31.9%, was deducted from the total efficiency, a rather low photocatalytic COD removal efficiency, 20.5%, was obtained. With increasing airflow, the COD removal efficiency first increased and then decreased slightly. A maximum COD removal efficiency, 86%, was observed at $0.06\,m^3\,h^{-1}$ airflow. Apparently, the promotion of air can be attributed to the role of oxygen in air, in addition to the role of speeding mass transportation of air due to its agitation. As for slight decrease in the rate constant of COD removal after $0.06\,m^3\,h^{-1}$, we tentatively presume that the result was involved in the reduction of residence time of O_2 at the TiO_2 surface with increasing airflow. Further work is needed to verify the view. However, it can be certain presently that a suitable airflow should be selected to obtain a higher COD removal efficiency.

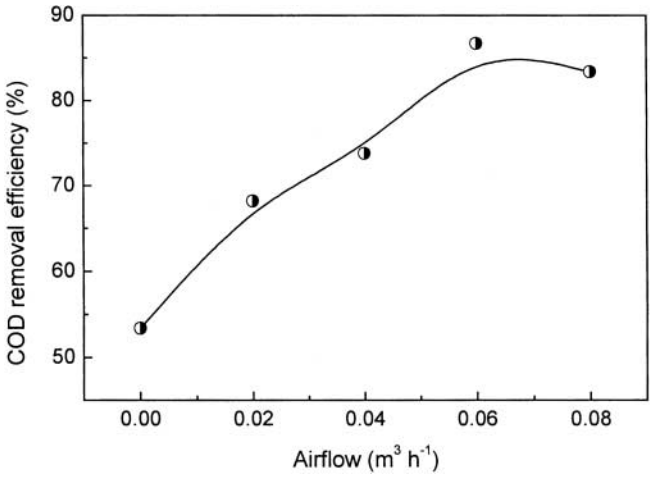

Figure 5. Dependence of COD removal efficiency on airflows.

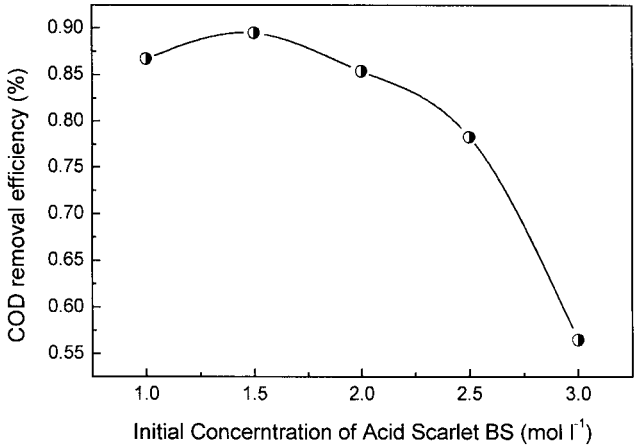

Figure 6. Dependence of COD removal efficiency on the initial concentration of Acid Scarlet BS.

Effect of Initial Concentration

It is also observed that the COD removal efficiency is dependent on the initial dye concentration. As shown in Fig. 6, the COD removal efficiency first increases slightly and then decreases significantly with increasing initial dye concentration. Many investigators have also observed that apparent rate constant was a function of initial substrate concentration in photocatalystic reaction but they could not give the reason. Wei explained well the similar phenomena observed in photocatalytic degradation of phenol in the term of the competitive adsorption between OH^- and

organic compound.[14] More recently Leng et al.[15] interpreted the decrease in apparent rate constants with the concentration of substrate, aniline, by assuming that photoproducts competed for the site of TiO_2 surface with aniline.[15] The increase in rate constant observed in our experiment could be simply ascribed to the increase in utilization of TiO_2 active sites, before the saturation of TiO_2 surface was not achieved, with increasing dye concentration, more TiO_2 active sites could be used in the solution, resulting in an increase in the rate constant. However, the reduction of rate constant at higher dye concentration, in addition to the above two reasons mentioned by Wei.[14] and Leng et al.[15] may be still due to that the transparency of dye solution is dramatically weakened, leading to the considerable reduction of the transmission intensity of ultraviolet light, when the dye concentration is increased, similar to the observations in the slurry photocatalytic process.[16]

Effect of Initial pH Value

It is well known that, for charged substrates, pH value has a significant effect on photocatalytic degradation of organic pollutants although the effect of pH value on photcatalytic efficiency for neutral substrate is rather insignificant.[16] For this PHP reactor, the COD removal efficiency from the solution containing-Acid Scarlet BS is found to be also heavily dependent on the initial pH value. As show in Fig. 7, in the range of lower than about 4.5, the COD removal efficiency increases with increasing pH, then apparently decreases when initial pH value is over 4.5. This change trend is similar to Arslan et al.'s[16] but not to Zhang et al.'s observations in photocatalytic experiments.[17] The reduction in COD removal efficiency can be interpreted by the combination of the surface charge of TiO_2, nature of dye and their relations with pH value. It is because that the adsorption of dye onto TiO_2 is probably the first step in the process of the photocatalysis. The studied substrate, Acid Scarlet BS, is a kind of anionic dye. At low pH value, Acid Scarlet BS with negative charge can be adsorbed on the surface of TiO_2 with positive charges. However, after pH 4.5, the surface of

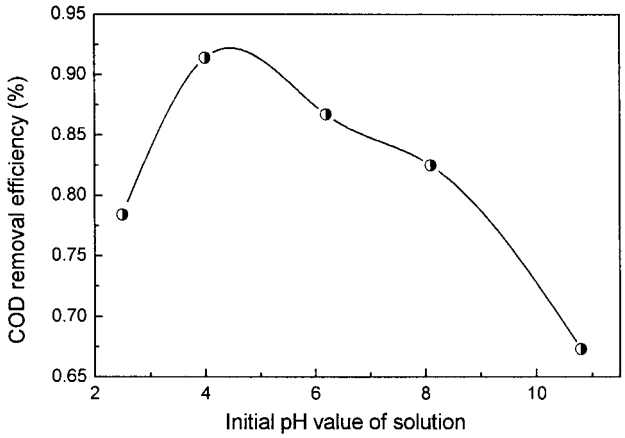

Figure 7. Dependence of COD removal efficiency on the initial pH value of the solution.

TiO_2 gradually becomes negatively charged. The adsorption of the dye onto TiO_2 becomes difficult due to the repellent effect of two species having same charges with increasing pH value. Therefore, the COD removal decreases as pH value is over 4.5. In addition, although the generation of hydroxyl radical, main reactive specie, is favoured by high pH values,[18] bicarbonate/carbonate, main photoproducts at high pH value, can effectively scavenge the hydroxyl radicals.[16] The scavenging effect may be another factor to reduce reaction rates.

Kinetics of COD Removal

It has been recognized that photocatalytic degradations of many organic pollutants could be fit with the Langmuir-Hinshlwood kinetics expression.[4] When the initial concentration of organic contaminates is low, the Langmuir-Hinshlwood rate form can be reduced an apparent first-order kinetic form.[19,20] However, with respect to environmental researchers, more concerns are paid to the reduction kinetics of total organic pollutants, i.e., initial organic pollutants and degraded intermediates that can be generally evaluated in the term of COD. As a result, we test to fit the COD reduction versus reaction time curve with a first-order kinetic form. An approximate linear function between $\ln(COD_t/COD_0)$ and reaction time t is found, as shown in Fig. 8. The apparent rate constant is obtained to be $0.03548\,min^{-1}$ from the slope of the curve.

Application of External Electric Field to PHP Reactor

Since Bard first found that the application of electric bias to a Pt anode coated with TiO_2 film could improve the efficiency of photocatalyic oxidation,[21] external electric filed has been frequently applied to photocatalytic degradation of organic pollutants and this process is referred to as photoelectrocatalysis in which external

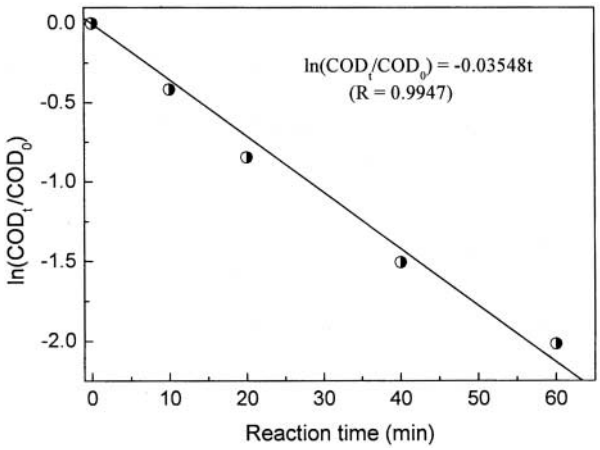

Figure 8. Curve of COD removal kinetics.

electric field could increase photocatalytic efficiency by driving away photogenerated electrons on TiO_2, suppressing the recombination of the photogenerated charges and subsequently increasing the lifetime of the active holes. In the present investigation, two metal Ti plates were placed in PHP reactor as cathode and anode, as shown in Fig. 1, in order to reform the photocatalytic reactor to an undivided photoelectrocatalytic reactor. A primary photoelectrocatalytic result is presented with the results of individual photocatalysis, electrooxidation and absorption in Figs. 9 and 10. It can be seen from these figures that the characteristic absorption of Acid Scarlet BS at 505 nm is disappeared in the photoelectrocatalytic

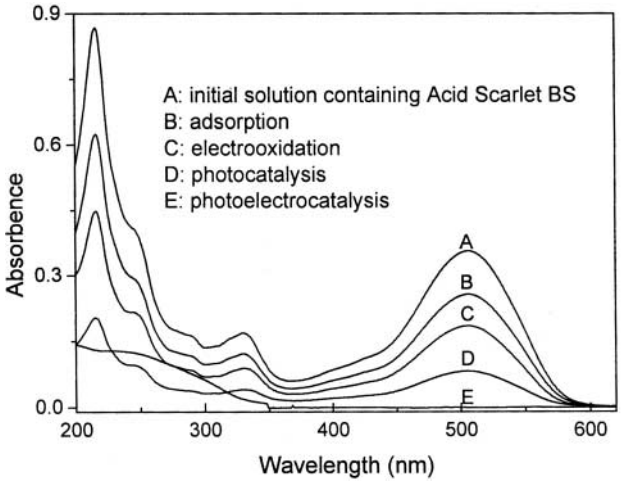

Figure 9. Change of UV vs. spectra for various processes.

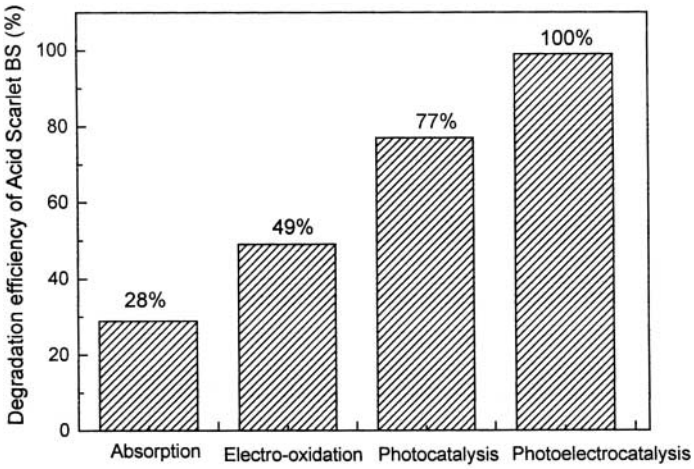

Figure 10. Degradation efficiencies of Acid Scarlet BS in various processes.

oxidation during 60 min (curve E in Fig. 9), implying the dye is completely degraded. The degradation efficiency researches 100%, higher 23% than that of individual photocatalytic process for an identical experimental time. However, Fig. 9 shows the absorbance in the range of about 230–380 nm for photoelectrocatalysis is higher than that for individual photocatalysis, suggesting that, in the two catalytic processes, the degradation mechanism of Acid Scarlet BS is different. Simultaneously, it is observed that the COD removal efficiency of the former was only slightly higher than that of the latter, not as unexpected. The observation is possibly associated with the higher absorbance in range of about 230–380 nm, however, more detail understanding of the observation needs to further investigations.

CONCLUSIONS

The following conclusions can be drawn from the investigation:

Degussa P25 TiO_2 could be immobilized on Ti particles without the change of crystal phase. This kind of TiO_2-coated Ti particles could be used as the packed materials of a packed-bed photocatalytic reactor. Inserting of hollow quartz glass tubes into the packed-bed photocatalytic reactor could apparently improve the photocatalytic efficiency of this photo-reactor. This improvement could be attributed to the increase in the penetrating depth of light into the packed-bed. The PHP reactor could efficiently remove COD from the simulated dye wastewater containing Acid Scarlet BS. However, the COD removal efficiency was considerably dependent on the operating parameters, airflow, initial dye concentration and initial pH value of solution. Application of external electric filed to PHP reactor could apparently increase the degradation efficiency of Acid Scarlet BS, but not considerably promote the COD removal.

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