



Photocatalytic degradation of textile dyes on Cu₂O-CuO/TiO₂ anatase powders



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ABSTRACT

TiO₂ anatase photocatalysts with ca. 2, 4 and 8 wt.% copper metal loading have been employed for the photocatalytic degradation of textile dyes (one of the major contaminants in effluent from textile industries around the world) and their degradation efficiencies compared with benchmark Degussa P25. In order to investigate their surface and bulk composition, all catalysts were characterized using XRD, UV-vis, XPS and TEM techniques. TEM and XPS results confirmed the presence of Cu in its oxide form (Cu₂O-CuO). Under optimized conditions (i.e. catalyst dose of 125 mg L⁻¹ and initial dye concentration of 5 mg L⁻¹), Degussa P25 showed 76% degradation efficiency for primary reactive blue 49 (RB 49) dye in 80 min. However, under the same optimized conditions, a complete primary RB 49 dye removal was observed at ca. 4 wt.% Cu₂O-CuO/TiO₂ catalyst. Kinetics analysis of photodegradation (*k_d*) nearly followed a pseudo-first-order kinetic model with a regression coefficient (*R*²) value in the range of 0.97–0.86 for 4 wt.% Cu₂O-CuO/TiO₂ catalyst. These results indicate that non noble supported TiO₂ anatase may be a better choice for photocatalytic dye degradation as compared to other commercially available photocatalysts.

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1. Introduction

The discharge of synthetic and chemically active dyes in to industrial wastewater is a major environmental concern due to their carcinogenic nature [1]. Further, the development of color due to the presence of these dyes can block sunlight and decrease oxygen dissolution resulting in low photosynthetic activity for aquatic biota [2]. It is, therefore, direly important to treat these colored effluents before they enter into aquatic bodies. Azo dyes are the largest group of synthetic dyes and are characterized by nitrogen to nitrogen double bonds (—N=N—). Azo dyes are currently used in a diverse range of industries including paper, textile, food, additives, cosmetics, xerography, laser materials and laser printing industries [3]. It should be noted that nearly 15% of world's overall toxic chemicals including dye products are directly disposed into the natural environment without any prior treatment [4,5].

Several treatment approaches have been reported in literature regarding decontamination and handling of colored effluents such as ion flotation [6], coagulation [7], adsorption [8], and sedimentation [9]. However, all of these techniques end up in producing secondary waste product which needs further treatment. To combat this issue, a relatively new and promising set of techniques, called Advanced Oxidation Processes (AOPs) have been developed and employed for dye contaminated industrial effluents treatment. Heterogeneous photocatalysis, a promising approach of AOPs, has successfully been developed and improved in recent years for better treatment of dyes in effluents [10,11]. AOPs are considered clean technologies for the treatment of polluted waters that apply the concept of producing hydroxyl radicals (HO^{*}) that attack the organic pollutants. The efficiency of AOPs is based on the generation of these highly reactive radicals that are unselective and powerful oxidizing species (*E*_o = 2.80V) and can degrade indiscriminately micro-pollutants with reaction rate constants usually around 10⁹ L mol⁻¹ s⁻¹ yielding CO₂, H₂O and inorganic ions as final products. A higher biodegradability and/or lower toxicity of the reaction byproducts, in comparison with the parent compounds, are desirable benefits of applying AOPs to treat wastewaters. AOPs can be applied as post-treatment or

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pre-treatment of biological processes. The integration of different AOPs in a sequence of complementary processes is also a common approach to achieve a biodegradable effluent that can be further treated by a cheaper and conventional biological process, reducing the residence time and reagent consumption in comparison with AOPs alone [11]. Conventional AOPs can be classified as homogeneous and heterogeneous processes, depending on whether they occur in a single phase or they make use of a heterogeneous catalyst like metal supported catalysts, carbon materials or semiconductors such as TiO_2 , ZnO , and WO_3 . While homogeneous processes are characterized by chemical changes depending on the interactions between the chemical reagents and target compounds only, heterogeneous processes also depend on the adsorption of reactants and desorption of products that occur at the active sites of the catalyst surface. As the reaction occurs, the products are desorbed and new species can adsorb on the active sites, so that the surface characteristics and the pore structure of the catalyst strongly affect catalysts efficiency and stability [12]. One of the AOPs is a photocatalysis process which involves the complete photo-mineralization or oxidation by generation of hydroxyl radicals that reacts with most of the organics and mineralizes them into CO_2 , H_2O and inorganic ions including PO_4^{3-} , NO_3^- , and halide ions without further production of intermediate toxic byproducts [13,14]. Photocatalytic degradation generally involves the complete photo-mineralization or oxidation of the target contaminants into H_2O , CO_2 . Among numerous types of heterogeneous photocatalysts, TiO_2 mediated photocatalytic oxidation has received much attention owing to its strong oxidizing power, long-term photostability and non-toxicity [15].

Nevertheless, TiO_2 possesses oxidizing property that can degrade contaminants efficiently, it has a large band gap (it can only be excited under UV photons) and fast charge carrier recombination limiting its practical application. About 4–5% of the entire solar spectrum falls within UV range that can excite TiO_2 based catalysts to exhibit photocatalysis with relatively lower activities [16–19]. To overcome these limitations, researchers have coupled a variety of semiconductors, metals, noble metals and non-metals with TiO_2 . These strategies can not only bring part of absorption in visible light region but also reduce charge carrier recombination due to Schottky barrier formation at TiO_2 -metal interface [19,20]. For example, incorporation of transition metals into crystal structure of TiO_2 may result into narrowing the band gap by shifting the absorbance towards the visible region [19]. Cu (II) has been reported to improve photocatalytic activity by modifying TiO_2 valence band spectrum and widening the visible light absorption ability. Chiang and co-workers [21] studied the photocatalytic activity of photodeposited CuO onto the surface of Degussa P25 particles to oxidize cyanide. It was found that CuO resulted into red shift of absorption spectrum of TiO_2 . However, possible limitations of such modifications can be photo-corrosion and recombination of prompted charges at metal surface [19].

The detailed investigations regarding TiO_2 coupled with non-noble transition metals mediated photodegradation is important for enhancing the overall dye treatment process at affordable cost. This study has been designed with an aim to evaluate the efficiency of Cu supported TiO_2 based photocatalysts for efficient degradation of textile dyes under controlled environmental conditions. The experimental parameters involved in controlling the extent of dye photodegradation reaction have been systematically evaluated.

2. Experimental

2.1. Catalyst preparation

TiO_2 anatase (Anatase >99%, crystalline size 2–10 nm) and copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99.0% purity) were purchased from

Sigma Aldrich while Degussa P25 was obtained from Evonik industries AG (63403Hanau), Germany. Ammonium hydroxide (NH_4OH , ACS reagent, 28.0–30.0% NH_3 basis) and 0.1 M HCl (HCl, ACS reagent, 37%) were used for pH controlled experiments. All reagents used were of analytical grade and were used without any further purification. Copper was deposited on TiO_2 nanoparticles using a combination of impregnation and precipitation-deposition method [22]. Briefly, 1 g of TiO_2 (Anatase) and predetermined amount of CuCl_2 salt for 2, 4, 8 wt.% Cu loadings were thoroughly dissolved in 100 mL of deionized water and kept at room temperature for 24 h to allow Cu ions to impregnate into TiO_2 . Then the solution pH was raised to 8.5 using NH_4OH solution. The final solution was stirred for one hour at 80 °C and allowed to stabilize for 24 h at room temperature. The solution was agitated and filtered (Grade 2 filter paper, Whatman; particle retention 8 μm) and the obtained precipitates were repeatedly washed with deionized water. Catalysts were dried at 90 °C for three hour and annealing at 400 °C for two hours.

2.2. Characterization technique

Powder X-ray diffraction (PXRD) spectrum of bare, Cu supported TiO_2 anatase and Degussa P25 composites were obtained on a Shimadzu XRD-6000 instrument by using Cu-K α radiation ($\lambda = 1.52 \text{ \AA}$) operating at a generator voltage of 40 kV and an emission current of 40 mA. X-ray diffraction patterns were acquired over 2θ range of 10–80° at a sampling scan width of 5°/min and a step time equal to 0.5 s [23]. Dimensional morphology and size of synthesized Cu supported TiO_2 and commercially available Degussa P25 were measured using Philips model PW 6030CM12/STEM electron microscope operating at 120 kV with filament emission current of 10 mA.

XPS spectra of photocatalysts were collected on a Kratos Axis Ultra spectrometer using monochromatized Al K α X-rays ($h\nu = 1486.6 \text{ eV}$) equipped with a hemispherical electron energy analyzer operated in the hybrid lens mode at 90° take off angle with respect to the specimen surface. The binding energy scale was calibrated using adventitious hydrocarbon referencing ($\text{C}1s = 285.0 \text{ eV}$). Survey spectra were collected at an analyzer pass energy of 80 eV over the binding energy range from 0 to 1200 eV (5 sweeps/25 ms dwell time). The relative concentration of the identified elements were calculated using peak areas of Ti2p, O1s and Cu2p core level signals. Relative sensitivity factors, based on instrument modified Schofield cross-sections were used in the quantification procedure (7.81, 2.93 and 25.39 respectively). The chemical states of Ti, O and Cu were determined from narrow scan spectra taken at pass energy of 20 eV over the Ti2p, O1s, and Cu2p regions (30 sweeps/150 ms dwell time), respectively.

2.3. Photodegradation experiments

Three synthetic textile dye samples including C.I Reactive Blue 49 (RB 49), C.I Reactive Red 24 (RR 24) and C.I Reactive Yellow 160 (RY 160) were obtained from Sundar Industrial Estate (SIE) textile garment zone, Lahore, Pakistan (C.I. = Colour Index). Table 1 shows the physio-chemical characteristics of textile dye samples. The chemical structures of dyes are given in Fig. 1.

Photocatalytic reactions were carried in an open top rectangular Pyrex photoreactor having 2.5" (Height) \times 6" (Width) \times 12" (Length) dimensions placed in a bench top fume hood. UV irradiating tubes (length=12") were obtained from Phillips Company having an output potential $2 \times 5 = 30 \text{ W}$ at $\lambda = 365 \text{ nm}$ and were assembled at a distance of 12 cm from the Pyrex reactor containing reaction solution. UV-vis spectrophotometer (DR5000TM, Hach Company, USA) was used to monitor the dye degradation or removal process. Typically, during the course of

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