

Cyclic reaction network modeling for the kinetics of photoelectrocatalytic degradation

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ABSTRACT

Among various advanced oxidation processes (AOPs) employed for the destruction of pollutants, photocatalysis has witnessed a tremendous development over the past two decades. Studies have reported the recombination of valence band holes and conduction band electron as a barrier in achieving higher degradation rate. To avoid recombination, an external bias can be applied to keep the charge carriers i.e. holes and electron separated. The present work investigates the synergistic effect of photocatalysis and electrocatalysis. A reaction network model is also developed for obtaining better insights of underlying complex processes. To validate the model, experiments were carried out for the anionic dyes with combustion synthesized TiO₂ as catalyst. The model has shown good agreement with the experimental findings. Loop coefficients were calculated in each case to have an estimate of hydroxyl radicals formed. Synergy, which is defined on the basis of first order rate constants, was observed in all cases of photoelectrocatalysis and increased with applied bias.

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Introduction

Synthetic dyes are widely used in many industries such as textile, leather, and paper production. The annual dye production exceeds 7×10^5 tons [1–3]. In order to protect the environment from serious threats of organic pollutants such as dyes, agro wastes, volatile organic compounds, detergents and surfactants, photocatalysis has been used over the past two decades [4]. The advantage of photocatalysis is the destruction of pollutant rather than its transfer to another media [5–11]. Essentially being an oxidation process, it exhibits the use of hydroxyl radicals (OH[•]) which has higher oxidation potential (2.8 V) as compared to atomic oxygen (2.42 V), ozone (2.07 V), hydrogen peroxide (1.78 V), permanganate (1.67 V) [1,12,13]. Moreover, these oxidizing agencies destruct partially and can cause secondary pollution [3].

The mechanism of photocatalysis illustrates that recombination of valence band hole and conduction band electron not only reduces the formation of hydroxyl radical but the heat generated also leads to desorption at the occupied sites [10,14–17]. The recombination can take place at surface or in volume [18]. To

improve the removal rate of organics from wastewater, the coupling of photocatalysis with other AOPs such as sonocatalysis, ozonation, electrocatalysis, Fenton and membrane processes has been extensively studied [19–24]. Electrocatalysis coupled with photocatalysis ensures the separation of photogenerated charge carriers by the application of external bias [25,26]. In order to minimize the recombination rate (and hence increase the lifetime), photoelectrocatalysis (PEC) is a convincing strategy. The external bias navigates the conduction band electron either to a non-photoactive electrode (counter electrode such as Pt) through a wire or from a surface site to a point, where an electron acceptor can be reduced [27,28]. The idea of increased recombination lifetime when the charge carriers are separated efficiently has been proposed [29].

In a recent study, the mechanism of photocatalysis and photoelectrocatalysis is elucidated with a special emphasis on the effect of cocatalyst [30]. Shang et al. have examined electric-agitation-enhanced photodegradation of rhodamine blue using planar ITO/TiO₂/ITO device at 1.5 V bias [25]. The increased rate constant for phenol degradation with potential has also been reported [31]. The problem of low efficiency involved in designing reactor for wastewater remediation and the use of tungsten electrode has been suggested [32]. The coupling of photoelectrocatalysis with cationic exchange membrane processes has shown enhanced reduction of Cr (VI) and improved oxidation of

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EDTA [33]. A slurry reactor has also been used to carry out the PEC in which the catalyst is taken in the suspension form [34,35].

The present work examines the degradation of different classes of anionic dyes like Orange G (mono azo), Indigo carmine (indigo), Alizarine cyanine green (anthraquinonic), Amido Black (AB) and Methyl Blue (triaryl methane) using combustion synthesized TiO_2 as catalyst in slurry reactor. We have investigated the synergistic effect of photocatalysis and electrocatalysis. A network model is also proposed, which reflects the general kinetics of degradation process. Thus, an integral form of rate expression obtained was used to interpret the concentration variation during electrocatalysis (EC), photocatalysis (PC) and photoelectrocatalysis (PEC) process for each dye.

Experimental

Materials

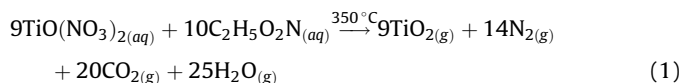
Analytical grade titanium tetra isopropoxide (TTIP – Alfa Aesar), glycine ($\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$ – S.D. Fine Chemicals), nitric acid (HNO_3 – Merck India) were used for catalyst synthesis as received. The dyes, alizarine cyanine green (ACG), methyl blue (MB), were obtained from Merck, India and orange G (OG), amido black (AB) from S.D. Fine Chemicals, India and indigo carmine from Rolex labs, India. All chemicals were used without any further purification. Double distilled Millipore filtered water ($0.22 \mu\text{m}$) was used for all purposes.

Preparation of catalyst

Nano size anatase TiO_2 was synthesized by solution combustion method [36–38]. In the typical synthesis process, 20 mL of TTIP was mixed with 80 ml cold distilled water under vigorous stirring. White precipitate of titanium hydroxide was separated and then

mixed with 1:2 nitric acid (by volume) till it gets completely dissolved. Resulting transparent solution is titanyl nitrate with small quantity of unreacted reactants.

Based on the concentration of titanyl nitrate in the solution, the stoichiometric amount (to maintain oxidizer to fuel ratio 1) of glycine (fuel) required for 100 mL of aqueous solution of titanyl nitrate (oxidizer) was 0.7346 g. The reaction is as follows



The stoichiometric amount of oxidizer and fuel was kept at 350°C in a preheated furnace for 10 min. The combustion was smoldering type. The product was ground to obtain a fine powder of anatase TiO_2 (CS TiO_2).

Degradation experiment

The schematic diagram of set up as shown in Fig. 1, consists of an UV radiation lamp (125 W, Philips, India) surrounded by quartz tube ($3.8 \text{ cm i.d.} \times 4.5 \text{ cm o.d.} \times 21 \text{ cm height}$). Another quartz beaker (4.5 cm i.d. and 7.5 cm height) contains the dye solution and kept in front of UV lamp. The electrocatalysis, photocatalysis and photoelectrocatalysis were carried out separately with the help of switches K_1 and K_2 .

Each dye was dissolved in water and degraded at its natural pH so as to avoid the effect of externally added anions or cations. The initial dye concentration was 50 mg L^{-1} and catalyst concentration was 1 g L^{-1} in all the experiments. The dye solution was kept in dark for 30 min in the presence of catalyst to attain adsorption–desorption equilibrium. All degradation experiments were carried out for a maximum of 2 h. In order to avoid heating, water was circulated through the lamp jacket. The solution was continuously stirred at 600–700 rpm to maintain the homogeneity throughout the solution.

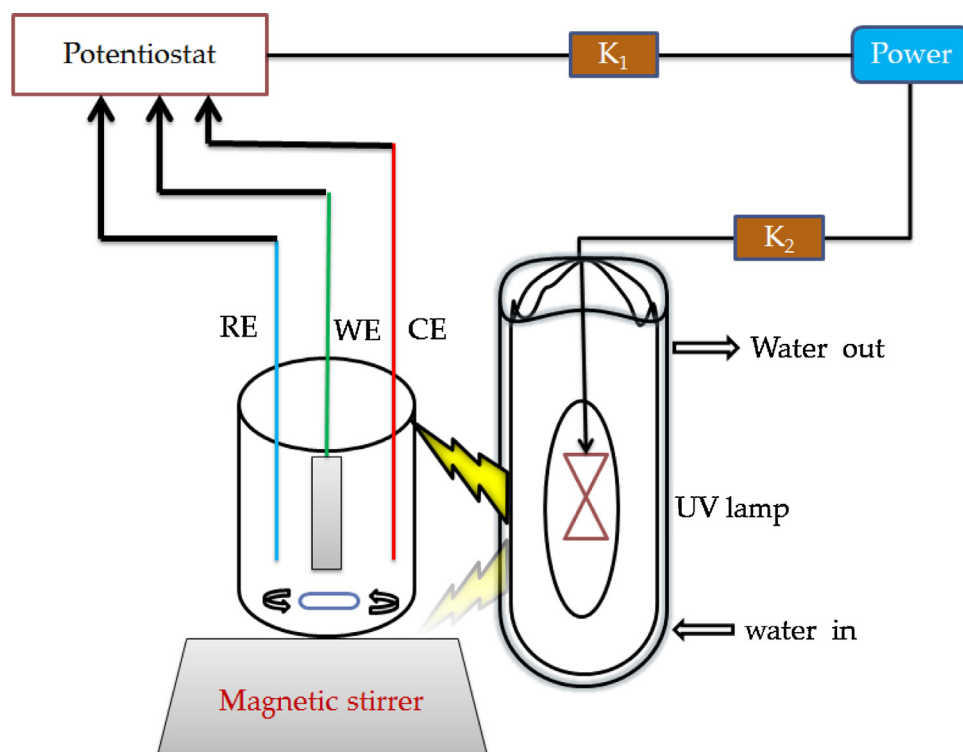


Fig. 1. Schematic of experimental set up for degradation experiment.

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