Preparation and application of nano-TiO_2 catalyst in dye electrochemical treatment

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Abstract

This paper reports results of an investigation into the removal of ARB (Acid Red B) dye in an electrochemical oxidation reactor with semi-conductor suspended in the electrolyte. TiO_2 nano-powders spiked with various elements, including Si, Co, Zn, La, Ag, Ce, W and Bi, were prepared by sol-gel method to improve colour removal efficiency. Through the $L_{16}(4^4)$ orthogonal experiment, the optimised preparation conditions of nano-TiO_2 catalyst were obtained, namely prepared at 400ºC and spiked with 10% Co(in molar ratio). The XRD (X-ray diffraction) analysis indicated that TiO_2 prepared at 400ºC occurred predominantly in the anatase crystalline form and the particle size was below 20 nm. The BET (Brunauer, Emmet and Teller) surface area was 69.2m^2/g. The decolourisation efficiency using Co (10%)/TiO_2 as catalyst was 33.1% and increased by 5.7% (about 1.21 times) compared with the colour removal without catalyst. The DRS (diffuse reflectance spectroscopy) demonstrated that the improvement of colour removal of Co(10%)/TiO_2 compared with pure TiO_2 was probably due to its better light absorption and photocatalytic activity in the visible region.

Keywords: electrochemical oxidation; titanium dioxide; Acid Red B; wastewater treatment

Introduction

Increasingly, electrochemical technology is receiving more and more attention, for its success in removing colour without the production of a secondary pollutant and due to its convenience and simplicity (Chen XJ et al., 2005; Chen XM et al., 2003; Chen GH, 2004; Brillas and Casado, 2002; Wang et al., 2004). The exact mechanisms, which occur during the electrolysis, are complicated and not entirely clear. Based on the intermediate products and radicals that can be determined in the electrolysis, such as O_3, H_2O_2, Cl_2, O_2, $\bullet OH$, ClO^- and other oxidants, it is postulated that organic pollutants could be oxidised directly or indirectly (Chen GH, 2004; Panizza and Cerisola, 2001).

However, the high energy consumption of electrochemical oxidation process confines its utilisation to a large scale. It is herewith reported that the presence of a catalyst in the electrical field can enhance the treatment efficiency. Chen WG (Chen WG and Zhu, 1998) has used metal dioxide to remove three types of organic pollutants, phenol, phenylamine and di-mephthalate from wastewater. The presence of H_2O_2 and ·OH was verified during the electrolytical catalysis process. The results showed that the removal efficiency depended on the reactive intermediate yield in the system. Organic pollutants were effectively removed by increasing the H_2O_2 yield. Notable removal efficiency was reached when the H_2O_2 yield was more than 0.3 mg/ℓ. A semiconductor catalyst can be used in electrochemical processes as well as in a photo-degradation system (Qamar et al., 2005; Shen et al., 2002). The removal of xenobiotic compounds, such as chlorophenols and pesticides, from municipal and industrial wastewater is very important because of their toxicity and their bioaccumulation tendency. Among the several methods proposed, photo-degradation catalysed by suspending inorganic semiconductors (i.e. TiO_2) has lately received wide attention because this process leads to non-toxic final products and shows high degradation efficiency (Lo et al., 2004; Bessekhouad et al., 2004). TiO_2 is a semiconductor catalyst that has been widely studied since the seventies and over the past century. The TiO_2 electrode has been used to degrade 4-chlorophenol and dyes (Azzam et al., 2000; Carneiro et al., 2004). In our previous study (Shen et al., 2002) it was shown that pure TiO_2 could not achieve successful catalytic results.

In the electrical field, many metal ions with variable valences, such as Fe^{3+} and Co^{3+}, are added to expedite the oxidation process by indirect oxidation. However, it is difficult to recycle these ions. Nano-composite TiO_2 mixed with metal ions with variable valences may have a higher catalytic effect. In order to study the effect of a semiconductor catalyst mixed with metal elements with variable valences in the electrical field, preparation and application of nano-composite TiO_2 catalyst have been studied in this research. The objective was to enhance the electrolysis efficiency.

Experimental

Preparation and characteristics of nano composite TiO_2 catalyst

Nano-composite TiO_2 catalysts were prepared through a proprietary sol-gel method. Tetrabutyl titanate and diethanolamine were dissolved in ethanol. After stirring for 2 h at room temperature, an ion additive was added to the sols, including cobaltous, cerous, lanthanum and tungstate salts etc. To this solution a mixed solution of water, nitric acid and ethanol was added with a burette while stirring. The ratio of $Ti(OC_4H_9)_4/C_2H_5OH/H_2O/HNO_3$ of this solution was 1:30:1:0.03 in molar. The resultant alkoxide solution was kept at room temperature for about 10 h after which it was heated at 400~700°C for 3 h. All the reagents

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