



Simultaneous photocatalytic removal of nitrate and oxalic acid over $\text{Cu}_2\text{O}/\text{TiO}_2$ and $\text{Cu}_2\text{O}/\text{TiO}_2\text{-AC}$ composites



Haruna Adamu^a, Alan J. McCue^a, Rebecca S.F. Taylor^b, Haresh G. Manyar^c, James A. Anderson^{a,*}

^a Surface Chemistry and Catalysis Group, Materials and Chemical Engineering, School of Engineering, University of Aberdeen, AB24 3UE, UK

^b School of Chemical Engineering and Analytical Science, The University of Manchester, The Mill, Sackville Street, Manchester, M13 9PL, UK

^c CenTACat, School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis road, Belfast, BT9 5AG, UK

ARTICLE INFO

Article history:

Received 24 February 2017

Received in revised form 29 May 2017

Accepted 30 May 2017

Available online 3 June 2017

Keywords:

Nitrate

Oxalic acid

Titania

Activated carbon

Composites

Photocatalysis

ABSTRACT

$\text{Cu}_2\text{O}/\text{TiO}_2$ (1–10 wt% Cu_2O) and 2.5% $\text{Cu}_2\text{O}/\text{TiO}_2\text{-AC}$ (2.5–20 wt% AC) photocatalyst composites were synthesised by an ethanol reduction method. The materials were characterised by a number of techniques which confirmed the presence of Cu_2O in contact with the TiO_2 . Pure TiO_2 alone was not active for the simultaneous photocatalytic removal of nitrate and oxalic acid under conditions employed, however, photocatalytic activity was observed for TiO_2 and TiO_2/AC in the presence of Cu_2O . This may have resulted from suppression of charge recombination *via* creation of a *p-n* heterojunction between Cu_2O and TiO_2 . Within the series, 2.5% $\text{Cu}_2\text{O}/\text{TiO}_2$ exhibited the best photocatalytic performance with 57.6 and 99.8% removal of nitrate and oxalic acid, respectively, with selectivities of 45.7, 12.4 and 41.9% to NH_4^+ , NO_2^- and N_2 , respectively after 3 h. For the carbon containing photocatalysts, 2.5% $\text{Cu}_2\text{O}/\text{TiO}_2\text{-2.5AC}$ displayed the highest activity with 42.5 and 96.6% removal of nitrate and oxalic acid, respectively, with 32.7, 11.6 and 55.7% selectivities to NH_4^+ , NO_2^- and N_2 , respectively. The highest AC loading tested resulted in selectivity to NH_4^+ of 21.6 with no NO_2^- detected, together with an improved N_2 selectivity (78.4%) albeit at lower (12.7%) nitrate conversion. Data suggests that $\text{Cu}_2\text{O}/\text{TiO}_2$ can be used in the photocatalytic reduction of nitrate and improved selectivity towards N_2 can be attained by influencing factors which control the relative rate of oxalic acid consumption.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Nitrate has become one of the most prevalent contaminants in groundwater, which originates from intensive agricultural activities, poor urban sewage management and waste disposal, as well as industrial effluents [1] and is seen as a serious global problem [2]. Organic pollutants are present in wastewater discharge from different industries including textiles, plastic, refinery, petrochemical, pharmaceutical, agrochemical and pulp and paper and may co-exist with nitrate [3,4]. Oxalic acid and other short organic acids are most likely to exist as intermediates following biological mineralisation of large organic molecules [3] and/or as one of incomplete mineralisation products of advanced oxidation treatments (AOT) [5].

Photocatalysis includes scope to simultaneously destroy residual organics and reduce inorganic ions such as nitrate from aqueous

solution [5] and are adjudged as a viable and promising technology for water pollution remediation [6]. TiO_2 is the most commonly explored photocatalyst although some studies indicate that TiO_2 is inactive for such a redox process [7,8], while others suggest either low activity [9] or high activity but with over-reduction of nitrate to ammonia [10,11]. Surface modification of TiO_2 with metals has been shown to be an effective manner of improving the efficiency of the photocatalytic reduction of nitrate in water [7,9,11–24] often by creation of Schottky barriers which act as sinks for photogenerated electrons. This consequently suppresses electron-hole recombination, as well as causing a negative shift in the Fermi level of the deposited metal [25,26], leading to increased reductive power.

Alternatively, a number of studies indicate that n-type TiO_2 combined with p-type metal oxide semiconductor may form a heterojunction which serves as an effective way of retarding recombination [27–30]. From research to date, n-type TiO_2 combined with p-type Cu_2O shows promise and uses a low-cost metal compared to others such as Ag [31,32]. This approach has been shown to be effective for diverse applications including degradation of organics [32–35] and the production of hydrogen [30,36,37]. It has

* Corresponding author.

E-mail address: j.anderson@abdn.ac.uk (J.A. Anderson).

been reported that p-type Cu_2O has a band gap of 2.0 eV [38] and a conduction band edge of -1.64 V [37]. Therefore, $\text{Cu}_2\text{O}/\text{TiO}_2$ can be exploited in the photocatalytic reduction of nitrate in the presence of organic hole scavengers, since the conduction band (CB) of TiO_2 is situated beneath that of Cu_2O and thus, electron-hole transfer between the heterojunction is thermodynamically permitted. Photogenerated electrons can move from Cu_2O to TiO_2 while holes migrate from the valence band (VB) of TiO_2 to Cu_2O , and as a result, the photodegradation mechanism of nitrate and oxalic acid over such composite differ from that of copper metal supported on TiO_2 .

TiO_2 also suffers from an inherently low specific surface area and thus limited adsorption capacity because of crystallite growth during elevated calcination temperatures. Pre-adsorption of reactants, particularly the electron accepting species, on the photocatalyst surface is often deemed to be a prerequisite for rapid interfacial charge carrier trapping that leads to effective photochemical conversion [10]. It has been reported that coupling TiO_2 with activated carbon (AC) enhances photocatalytic degradation of pollutants because of increased adsorption capacity and improved interfacial charge transfer rate [39]. Such improvement in the photocatalytic efficiency of TiO_2/AC composites have been reported elsewhere [40–43]. In addition, the presence of activated carbon in $\text{TiO}_2\text{-AC}$ composites may influence the photodegradation reaction pathway by generating different intermediate species compared to TiO_2 alone [44]. In this study, $\text{Cu}_2\text{O}/\text{TiO}_2$ and $\text{Cu}_2\text{O}/\text{TiO}_2\text{-AC}$ photocatalyst composites were prepared and characterised and their ability to simultaneously photodegrade nitrate and oxalic acid assessed.

2. Experimental

2.1. Preparation of photocatalysts composites

All photocatalysts were prepared by an ethanol-based reduction method [30]. TiO_2 (Aeroxide P25, purchased from Sigma-Aldrich) was dispersed in anhydrous ethanol and stirred for 1 h before slow addition of the desired amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. After vigorous stirring for 2 h, the solvent was removed by drying at 60°C for 6 h and the resultant sample was subsequently calcined at 350°C for 2 h in air. The ethanol reduction method has been shown to produce materials with Cu loadings lower than the nominal values (more pronounced difference for higher loadings) [30]. Regardless, the as-prepared photocatalysts are denoted as x% $\text{Cu}_2\text{O}/\text{TiO}_2$, where x% represents nominal weight percent of loaded copper (1, 2.5, 5 or 10 wt%). Carbon containing $\text{Cu}_2\text{O}/\text{TiO}_2\text{-AC}$ composites were prepared following the same method except that the desired amounts of activated carbon (AC) and TiO_2 were dispersed in anhydrous ethanol and stirred vigorously for 1 h before slow addition of the desired amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. The resulting composites were labelled as 2.5 $\text{Cu}_2\text{O}/\text{TiO}_2\text{-yAC}$ (2.5 wt% was deemed to be the optimum copper loading – see later) where y reflects the loading of activated carbon (2.5, 5, 10 and 20 wt%) in the composites.

2.2. Photocatalysts characterisation

The X-ray diffraction pattern of the photocatalysts was examined using an X'Pert Pro Diffractometer (PANalytical) with a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.15418$ nm) in the range $5\text{--}80^\circ 2\theta$. Textural properties (surface area, pore volume and pore size) were determined by collecting N_2 adsorption-desorption isotherms at -196°C on a Tristar-3000 instrument (Micromeritics). The optical properties of the photocatalysts were studied using a UV-vis spectrometer (Cary 60, Perkin-Elmer) in diffuse reflectance mode using a 60 mm diameter integrated sphere and BaSO_4 as the internal reference standard. To establish whether Cu influenced the band gap

of TiO_2 in the photocatalysts, plots of $(\alpha h\nu)^{1/2}$ versus E_{photon} was applied by fitting the absorption data to the equation. Reducibility of the copper component of the photocatalysts was investigated by temperature-programmed reduction (TPR) using a TPDRO 1100 instrument equipped with TCD detector. Samples were heated from 40 to 600°C at $5^\circ\text{C}/\text{min}$ in a 5% H_2/N_2 mixture. The amount of hydrogen consumed was quantified based on a response factor determined using a CuO reference standard. The nature of exposed sites on the copper component was probed by studying the adsorption of CO by FTIR (Perkin-Elmer 1750 series spectrometer). The sample was pressed into a self-supporting disc and held in a quartz holder in a vacuum line which allowed for heating, evacuation and controlled gas manipulation. Samples were first outgassed and heated to 120°C to remove surface water. The sample was then cooled to beam temperature and outgassed to a residual pressure of $ca. 4 \times 10^{-5}$ Torr before an initial spectrum (25 scans, 4 cm^{-1} resolution) was collected prior to exposure to increasing CO overpressures (0.3–40 Torr). Results are presented as difference spectra relative to the initial scan collected before exposure to CO.

XPS measurements were carried out using a Kratos AXIS Ultra DLD XPS spectrometer with monochromated $\text{AlK}\alpha$ X-rays and hemispherical analyser with a pass energy of 160 eV. The powdered samples were mounted on copper tape and binding energies were normalised to the C 1 s signal from adventitious carbon at 284.6 eV. Background subtraction was performed using a Shirley background and Casa XPS [45].

2.3. Photocatalytic tests

Photocatalytic reactions were carried out in a stirred, batch reactor fitted with a primary cooler (Fischer Scientific 3016S) to maintain the reaction temperature at 25°C . A secondary cooling system was also incorporated to control heat given out by the 400 W UV lamp (Hereaus BQ 512 E, 400 W, 230 V and a maximum wavelength of 365 nm). Water was used as the coolant in this secondary cooling system by running a constant flow through a Pyrex cooler which encased the UV lamp. The Pyrex glass sleeve also functioned to filter out the light of wavelengths less than 290 nm which might otherwise lead to direct photolysis of nitrate and oxalic acid. Therefore, only light in the range between 290 and 365 nm were available for experiments conducted (Figure SI-1). In the experimental design, initially, 1.0 g/L photocatalyst composite was stirred in 1.5 L of ultra-pure water and N_2 bubbled for 30 min to displace dissolved oxygen. Thereafter, 100 mL stock solutions of nitrate (100 ppm) and optimal oxalic acid concentration (0.005 M) were added to the suspension. The reactor was stirred for another 1 h in the dark, which was determined to be beyond the minimum time required to ensure adsorption-desorption equilibrium was established. A sample was then taken to determine the equilibrium concentrations of the model pollutants in solution before the light was turned on ($t = 0$). During the photocatalytic reaction test, samples were withdrawn with a $0.45\ \mu\text{m}$ syringe filter at fixed time intervals over a 3 h reaction period. The net concentrations of nitrate and oxalate, as well as nitrite (one of the by-products of nitrate reduction), were measured using ion chromatography (Dionex DX-120), while ammonium was measured using a Merck Spectroquant ammonium test kit which follows the indophenol test for ammonium [46]. Thereafter, the degradation (%) of both model pollutants was calculated using Eq. (1).

$$\text{Degradation}(\%) = \frac{C_t}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration at zero time, and C_t is the concentration after a particular period of illumination. The selec-

Download English Version:

<https://daneshyari.com/en/article/6453932>

Download Persian Version:

<https://daneshyari.com/article/6453932>

[Daneshyari.com](https://daneshyari.com)