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Recyclable immobilized carbon coated nitrogen doped TiO_2 for photocatalytic degradation of quinclorac under UV–vis and visible light

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ABSTRACT

The removal of quinclorac (QNC) herbicide through photocatalysis reaction under UV–vis and visible light irradiations is described. Immobilized carbon coated nitrogen doped TiO_2 ($CNTiO_2$/EP) was employed as photocatalyst and the photodegradation was done with the addition of H_2O_2. The optimization studies revealed that the best removal of QNC was obtained at pH 3 with the addition of 30 μL of H_2O_2. As much as 94% and 87% of QNC was removed after 90 min under UV–vis and visible light exposure, respectively. Additionally, 67% mineralization of 20 mg L^{-1} of QNC was achieved after 12 h under UV–vis light while 42% of QNC was mineralized under visible light within a similar timeframe. The reusability test shows sustainable $CNTiO_2$/EP performance up to ten consecutive applications where the average removal of QNC was 92% and 72% under UV–vis and visible light, respectively.

1. Introduction

Quinclorac, QNC (3,7-dichloroquinoline-8-carboxylic acid) is a highly selective auxin herbicide which is used to control dicot and monocot weeds in paddy fields. The presence of QNC in the environment is considered as a potential groundwater contaminant since QNC is soluble in water (72 mg L^{-1}) with a hydrolysis half-life of 30 days [1]. QNC can also bind to soils with an aerobic soil half-life of 211 days [2]. Its extensive application may cause negative effects towards living organisms as it is harmful to the liver and kidney of mammals and also effects hydrophyte and aquatic creatures negatively [3].

Several studies have reported the removal of QNC via various degradation processes. Among the degradation processes, biodegradation using bacteria such as *Pseudomonas* sp. [4], *Arthrobacter* sp. [5], *Ochrobactrum* sp. [6] and *Stenotrophomonas* sp. [7] have frequently been favored. These bacteria have shown efficient biodegradation of QNC in which QNC serves as a carbon and energy source for the bacteria [6].

Other degradation processes include chemical degradation and advanced oxidation processes (AOPs). Recently, Shi et al. [8] synthesized gold nanocatalysts deposited on *Saccharomyces cerevisiae* for the effective chemical degradation of QNC. The degradation of QNC was carried out in the presence of sodium borohydride ($NaBH_4$). The obtained results suggest that the degradation of QNC relied on the concentration of $NaBH_4$, instead of the adsorption of QNC and the gold nanocatalyst alone. The catalyst was applied for three consecutive cycles. The efficiency of this catalyst decreased constantly each cycle due to the loss of gold nanocatalyst during the recovery process [8]. In contrast, the AOP method is favored for the degradation of organic pollutants as it is possible to completely mineralize the organic pollutants to water, carbon dioxide and inorganic ions [9]. As such, Zhong et al. [10] reported the degradation of QNC through oxidation utilizing sulfate radicals generated from the decomposition of peroxymonosulfate (PMS) in the presence of cobalt (II) ions in aqueous phase.

Photodegradation is an alternative method to degrade QNC. To date, Pareja et al. [2] employed TiO_2 for the photocatalytic degradation of QNC whereby most of the QNC degraded after 40 min. To our knowledge, the study by Pareja et al. [2] is the only work involving the degradation of QNC using TiO_2 photocatalysts. No study has been done to degrade QNC using nitrogen doped TiO_2 and immobilized TiO_2 systems. In addition, the utilization of visible light as the light source for the photocatalytic degradation of QNC has never been explored. Besides, the extent of mineralization of QNC and the possible reusability of the photocatalyst has yet to be understood.

To date, the work related to the removal of QNC via photodegradation process is still scarce. Therefore, the aims of this study are to degrade and mineralize QNC using immobilized carbon coated nitrogen doped TiO_2 ($CNTiO_2$/EP) and H_2O_2 system under UV–vis and visible light irradiations. This aspect has never been explored before as no work has reported the application of immobilized photocatalyst for photodegradation and mineralization of QNC. Besides, the optimization of operational parameters (e.g.: H_2O_2, pH and QNC concentration) for degradation of QNC, reusability of $CNTiO_2$/EP to degrade QNC in

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consecutive cycles and the proposed degradation pathway were also reported. It is worth to note that this is the first study which reports the degradation and mineralization of QNC under visible light irradiation.

2. Materials and methods

2.1. Materials and reagents

Epoxidized natural rubber (Kumpulan Guthrie Sdn. Bhd., Malaysia), polyvinyl chloride (Petrochemicals (M) Sdn. Bhd., Malaysia), Degussa P25-TiO_2 (Acros Organics, Belgium) and urea (Fluka-Garantie, Germany) were used in the fabrication of photocatalyst systems. Quinclorac (Sigma-Aldrich, USA) was used as the model pollutant. Sodium hydroxide, NaOH (Merck, Germany) and hydrochloric acid, HCl (Merck, Germany) were used to adjust the pH of QNC solution while H_2O_2 (QRëC, New Zealand) was applied for the photodegradation process. High performance liquid chromatography (HPLC) grade acetonitrile (QrëC, New Zealand) and acetic acid (Systerm, Malaysia) were used to prepare the HPLC mobile phase. Ultrapure water generated by Millipore Direct-Q™ 3 Ultrapure Water Purification System (Fisher Scientific, USA) was used to prepare the solutions and HPLC mobile phase.

2.2. Preparation and characterizations of $CNTiO_2$/EP

Details on the preparation and characterization of immobilized carbon coated nitrogen doped TiO_2 ($CNTiO_2$/EP) were explained in our previous work [11]. The formulation consisting of $CNTiO_2$ photocatalyst, epoxidized natural rubber-polyvinyl chloride (EP) polymeric binders and organic solvents was prepared and was coated on the surface of a glass support. The coating process was repeated several times until the desired photocatalyst loading was obtained. The $CNTiO_2$/EP was then photo-etched for 10 h in ultrapure water by exposing to a UV–vis light in order to create pores on the surface of immobilized photocatalyst and generate conjugated polyene from polyvinyl chloride.

The surface morphology of the $CNTiO_2$/EP was characterized using scanning electron spectroscopy (SEM) and N_2 adsorption desorption analyses. The SEM micrograph was obtained using a SEM (LEO SUPRA 50 VP Field Emission) microscope while the N_2 adsorption desorption isotherm was acquired from the Surface Analyzer Nova Quantachrome 2000. The functional groups present in $CNTiO_2$/EP was observed using Fourier Transform Infrared (FTIR, Perkin Elmer series 200) spectrometer with the scan ranging from 650 to 4000 cm^{-1}. Detailed results on the other characteristics of the catalysts was described in our previous report [11].

2.3. Photocatalytic degradation of quinclorac (QNC)

The experimental set-up used in this experiment is similar to our previously reported work [11]. Generally, 20 mL of 20 $mg\,L^{-1}$ QNC solution was placed in a glass cell (4.7 cm width x 6.5 cm height) containing a 2.29 $mg\,cm^{-2}$ $CNTiO_2$/EP coated glass plate. For photocatalytic degradation under UV–vis light, the glass cell was placed in front of a 45 W household compact fluorescent lamp (Philips Ecotone, model E27, 220–240 V, 50–60 Hz) as a light source. Meanwhile, the photocatalytic reaction under visible light was carried out by fitting a UV filter glass (Schoot GG420 UV-filter) in between the glass cell and fluorescent lamp in order to prevent the UV light from reaching the photocatalyst. The intensity of the UV–vis (UV: 2.9 $W\,m^{-2}$; visible: 400 $W\,m^{-2}$) and visible (UV: 0 $W\,m^{-2}$; visible: 350 $W\,m^{-2}$) light emitted from the fluorescent lamp was determined using a radiometer (Solar Light Co. PMA 2100 with UV-A, UV-B and PAR Quantum light sensor detectors). As much as 40 $mL\,min^{-1}$ of air was supplied into the glass cell during the experiment by using an aeration system consisting of aeration pump (model BB-8000), aeration tube and pipette. Samples of treated QNC solution were collected and subjected to HPLC to determine the remaining concentration of QNC. The HPLC system was equipped with a C18 column and its UV detector was set to 280 nm. A solution composed of 49.9% acetonitrile, 0.2% acetic acid and 49.9% ultrapure water was used as mobile phase.

Various operational parameters were investigated. The effect of H_2O_2 was determined by adding different amounts of H_2O_2 (0 to 40 μL) into the QNC solution prior to photocatalytic process. The study on the effect of pH was done by adjusting the pH of QNC solution from pH 3 to 8 using 0.1 M HCl or 0.1 M NaOH solutions prior to the photocatalytic degradation process. The influence of QNC concentration was investigated by varying the concentration of QNC from 10 to 60 $mg\,L^{-1}$. Finally, a comparison study on the removal of QNC by different photocatalyst systems was done by replacing $CNTiO_2$/EP with TiO_2/EP (2.29 $mg\,cm^{-2}$), suspended TiO_2 (0.07 g) and suspended $CNTiO_2$ (0.07 g).

The photocatalytic degradation of QNC was presented as percent of remaining and removed QNC as well as pseudo-first order rate constant. The pseudo-first order rate constant value was calculated by using a Langmuir-Hinshelwood equation (Eq. (1))

$$\ln (C_0/C_t) = kt \tag{1}$$

where C_0 is the initial concentration of QNC ($mg\,L^{-1}$), C_t is the concentration of QNC at time t ($mg\,L^{-1}$), t is the time of light exposure (min) and k is the first order rate constant for photocatalytic removal of pollutant (min^{-1}). The rate constant value was obtained by plotting ln (C_0/C_t) versus t which produced a straight line with the slope representing the k value. Meanwhile, the percent of remaining QNC were calculated using Eq. (2).

$$\%\ \text{remaining pollutant} = (C_t/C_0) \times 100\% \tag{2}$$

2.4. Mineralization of QNC

The mineralization of QNC by $CNTiO_2$/EP under UV–vis and visible light was carried out using a similar set-up as for the photocatalytic degradation of QNC. The QNC solution was irradiated for 12 h under UV–vis or visible light. The treated solution was collected every 2 h and subjected to total organic carbon, TOC (Shimadzu, TOC-LCPH/CPN) and ion chromatography, IC (Metrohm, model 792 Basic IC) analyses to ascertain the amount of remaining carbonaceous substances and the generated anion species, respectively.

2.5. Reusability of $CNTiO_2$/EP

The reusability and stability of $CNTiO_2$/EP for photocatalytic degradation of QNC under UV–vis and visible light was evaluated by employing the same $CNTiO_2$/EP photocatalyst plate to the successive treatment of 20 $mg\,L^{-1}$ of QNC solutions. The photocatalytic degradation was carried out at pH 3 with the addition of 30 μL of H_2O_2 in the presence of 40 $mL\,min^{-1}$ of air supply. After each cycle, the $CNTiO_2$/EP plate was regenerated in 20 mL ultrapure water with the same light exposure as the photocatalytic degradation process for 30 min prior to the successive cycles. The results for reusability test were presented as pseudo-first order rate constant and percentage of QNC removal.

3. Results and discussion

3.1. Characteristics of immobilized $CNTiO_2$/EP

The FTIR analysis of the $CNTiO_2$/EP (Fig. 1a) revealed absorption peaks at 3417 and 1630 cm^{-1} attributed to the stretching and bending bands of OH groups. This group originated from the adsorbed water on the surface of the photocatalyst [12]. The presence of water and