



Research article

Rapid photo-degradation of 2-chlorophenol under visible light irradiation using cobalt oxide-loaded TiO₂/reduced graphene oxide nanocomposite from aqueous media



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ABSTRACT

The photocatalytic removal of 2-chlorophenol (2-CP) from water environment was investigated by TiO₂-RGO-CoO. Cobalt oxide-loaded TiO₂ (TiO₂-CoO) supported with reduced graphene oxide (RGO) was synthesized using a sol-gel method and then annealed at 500 °C for 5 min. The material characteristics were analyzed by UV-Vis analysis, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. Incorporation of cobalt oxide and RGO into the TiO₂ system (TiO₂-RGO-CoO) lowered the band gap energy to 2.83 eV, which greatly enhanced the visible light absorption. The TiO₂-RGO-CoO photocatalyst showed complete removal of 20 mg/L 2-CP within 8 h with the addition of 0.01% H₂O₂ under 100 W visible light irradiation. The photo-degradation efficiency of 2-CP (10 mg/L) was 35.2, 48.9, 58.9 and 98.2% for TiO₂, TiO₂-RGO, TiO₂-CoO and TiO₂-RGO-CoO, respectively, in the presence of visible light irradiation at solution pH of 6.0. The TiO₂-RGO-CoO photocatalyst retained its high removal efficiency even after five photocatalytic cycles.

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1. Introduction

The 2-chlorophenol (2-CP) is widely used in the preparation of phenolic resins, pesticides, plastics, and paints. Chemical compound production, coal gasification, oil refining, oil production and petro-chemical wastewaters are the major sources of 2-CP in the environment. Exposure to 2-CP may cause carcinogenic and teratogenic properties in humans and the environment (Igbinsosa et al., 2013; Karci, 2014). Therefore, advanced and effective methods need to be developed to minimize or neutralize the environmental harm of 2-CP. Removal of phenolic compounds by photocatalytic degradation processes in the presence of UV and visible light is gaining importance because photocatalytic degradation offers economic treatment, great retentive capability, and effortless and great degradation efficiency only for limited use or scale (Li et al., 2015b; Ji et al., 2015; Liu et al., 2015).

Titanium dioxide (TiO₂) has been one of most attractive sorbents, photocatalysts and semiconductors for environmental remediation, due to its low cost, long-term stability and very low

toxicity for humans and the environment (Tian et al., 2014). Many investigations have reported the photocatalytic improvement in TiO₂ in UV regions. However, various difficulties remain for commercialization, such as response at limited light range and weak removal efficiency of organic pollutants in the photocatalytic system of TiO₂. In order to enhance the photocatalytic property in visible region, the doping of transition metals onto TiO₂ has been extensively examined (Dahl et al., 2014; Chen et al., 2015). Cobalt(II) with redox potential of 0.28 V (Co²⁺(aq) + 2e⁻ → Co(s)) has been found to be a good dopant to enhance photocatalytic activity in the visible region (Raji and Lombardi, 2015). The generation of electrons from the excitation of the photocatalyst is precisely trapped with Co²⁺, which releases the oxidation valence hole of the photocatalyst for photocatalytic removal of organic pollutant. During photocatalysis activity, electron-hole recombination is reduced due to charge trapping sites that are provided by the dopant metal ions (Miao et al., 2014).

Additionally, combinations of TiO₂ with mesoporous materials, such as zeolite, silica or carbon based materials are also capable of improving photocatalytic properties in the visible region (Nguyen-Phan et al., 2014; Dahl et al., 2014; Chen et al., 2015). Nowadays, graphene is one of the noble carbon-based materials for scientific

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research because of its great thermal, electrical and mechanical properties (Chen et al., 2012). The nanocomposite of TiO₂ supported with reduced graphene is a perfect combination to enhance the separation of charge during processes of electron-transfer because of the conjugated structure of graphene oxide (GO) (Dreyer et al., 2010). Recently, TiO₂ nanocrystal/reduced graphene oxide (TiO₂/RGO) hybrid synthesized by a sol–gel process was reported to enhance the electro-catalysis activity for microbial treatment (Zou et al., 2015). Tao et al. reported that a nanocomposite of graphene/TiO₂ nanotube showed photocatalytic degradation of acetaminophen from water pollutant (Tao et al., 2015). TiO₂ graphene composites were also reported for solar photocatalytic disinfection of water (Fernandez-Ibanez et al., 2015). In another example, a ternary nanocomposite of RGO/TiO₂/zinc oxide (Raghavan et al., 2015) and TiO₂/Cu₂O/RGO (Almeida et al., 2015) was also reported for enhancing the photocatalytic degradation of organic pollutants. Tang et al. reported the use of a recyclable composite of magnetic TiO₂-graphene for photocatalytic removal of herbicides from water (Tang et al., 2013).

Cobalt ions have high magnetic, optical and electrical properties but have generally been passed over for photocatalysis (Wang et al., 2004). Amna et al. reported that cobalt-doped TiO₂ nanofibers showed bactericidal effect (Amna et al., 2013). Cobalt/TiO₂-doped SBA-15 composite was also reported for dye degradation in visible light (Suraja et al., 2011). However, little research has been conducted to investigate the scientific knowledge incorporation of cobalt oxide (CoO) loaded TiO₂ further supported with GO. Thus the incorporation of cobalt ion loaded TiO₂ nanoparticles (NPs) on the surface of RGO might improve their photocatalytic effectiveness for removal of 2-CP under visible light irradiation from water environment.

To aim of this study is to investigate the effect of metals ion loading and modification with RGO for photocatalytic removal of 2-CP in the presence of visible light.

2. Materials and methods

2.1. Materials

Cobalt nitrate (Co(NO₃)₂·6H₂O) as a dopant, titanium (IV) isopropoxide (TIP) and natural graphite powders (99.9% carbon content) for the synthesis of GO were obtained from Daejung Chemical and Metals Co. LTD, South Korea. Double distilled H₂O was used for reagent preparation and all chemicals used were of analytical grade.

2.2. Preparation of TiO₂ NPs and cobalt oxide-loaded TiO₂ (TiO₂-CoO)

The TiO₂ NPs and TiO₂-CoO were prepared by modified sol–gel method with in-situ metal doping process. Cobalt nitrate (Co(NO₃)₂·6H₂O) was loaded in the TIP solution during the sol–gel method used to prepare TiO₂ NPs. In detail, glacial acetic acid (14.32 mL) was added in the TIP (7.44 mL) solution with the addition of 80 mL ethanol solution for hydrolysis. The solution was stirred for 20 min at 30 °C for complete hydrolysis. Then, the aqueous solution (80 mL) of cobalt nitrate (0.5 wt %) with double distilled water was mixed into the above TIP solution. A cobalt loaded TiO₂ solution with 0.5 wt% cobalt concentration was attained by adding NaBH₄ (2 mL of 0.5 M) at the time of cobalt-titanium solution mixing. The mixed oxide formation of cobalt oxide-doped TiO₂ was visually confirmed when the mixed solution color changed to speckled white in color. The above TiO₂ and CoO mixed solution was continuously stirred at 40 °C for 12 h for complete hydrolysis to obtain a mixture containing the gel.

Afterward, the gel-containing mixture was dried at 80 °C for 10 h and then annealed at 500 °C for 5 min to afford the cobalt-loaded TiO₂ composite.

The TiO₂ NPs were prepared using the above process at a similar condition with no addition of cobalt nitrate (Sharma and Lee, 2013).

2.3. Incorporation of TiO₂-CoO onto RGO (TiO₂-RGO-CoO)

The Hummers method was used to synthesize GO from graphite powder (99.9% carbon content) as reported earlier (Johra and Jung, 2015). For the synthesis of TiO₂-RGO-CoO nanocomposite, firstly, a mixture of solution A and solution B was prepared. For the preparation of solution A, GO suspension (20 mg of 4 mg/mL) and cetyltrimethylammonium bromide (CTAB, 0.5 g) was mixed in 30 mL of ethanol with stirring for 30 min. Solution B was a mixture of TIP (7.44 mL), glacial acetic acid (14.32 mL) and 120 mL cobalt nitrate (0.5 wt %) in deionized water placed in a 250 mL beaker. After 1 h stirring, sodium borohydride (2 mL of 0.5 M) was added drop wise into the cobalt-titanium mixture. The mixed oxide formation of cobalt doped TiO₂ was visually confirmed when the mixed solution color changed to speckled white. After solution B was added drop wise into solution A, 20 mL deionized water was also added followed by 12 h stirring and overnight drying in an oven at 80 °C. The dried compound was annealed under 500 °C for 5 min to obtain TiO₂-RGO-Co. GO was converted into RGO by annealing process at 500 °C (Tan et al., 2015).

TiO₂ NP-doped RGO (TiO₂-RGO) nanocomposite was prepared via the same process under identical conditions to those above except for no mixing of cobalt nitrate.

2.4. Material characteristics analysis

A UV–Vis spectrophotometer (UV-1700 Shimadzu) was used to analyze the changes in spectral region at 300–700 nm wavelengths and Nicolet Nexus 470 Fourier transform infrared (FTIR) spectroscopy was used to identify the functional groups of the nanocomposite. The crystallinity was checked at the 2θ range of 10–80° by X-ray diffraction (XRD, Bruker AXN). X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha XPS spectrometer) was used to identify the oxidation states of the elements. A scanning electron microscope (SEM) connected with an energy-dispersive X-ray (EDX) spectrometer was used to analyze the surface morphology and elemental composition of the nanocomposite. Transmission electron microscope (TEM) micrographs were obtained on a JEOL JEM 2100 electron microscope.

2.5. Photocatalytic experiment for 2-CP degradation

The photocatalytic activity was evaluated by measuring the removal of 2-CP at a concentration of 5–150 mg/L under fluorescent light irradiation. Photocatalytic processes were carried out in a thermostatic batch reactor equipped with Xe-lamps (Superstar Dulux EL, 20–200 W), which were used as a visible light source. For the photocatalytic test run, 50 mg of nanocomposite was added into 100 mL of the 2-CP solution and the pH was adjusted using 0.1 M HCl or NaOH. The reaction solution was exposing in the presence of visible light at room temperature before starting the reaction. At given time intervals, the solutions were centrifuged and filtered using whatman (0.45 mm) filter paper to remove the nanocomposite and then the filtrates were analyzed by using a UV–Vis spectrophotometer (Genesys 10S UV–Vis spectrophotometer, Thermo Scientific) at a wavelength (λ_{max}) of 273.2 nm (Ma et al., 2014). The effects of the experimental parameters, i.e., pH, 2-CP concentration variation, photocatalyst dose, H₂O₂ and power of visible light, on the 2-CP removal were examined. The used

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