Process Safety and Environmental Protection 95 (2015) 247–254

Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Detoxification of hexavalent chromium in wastewater containing organic substances using simonkolleite-TiO_2 photocatalyst

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ARTICLE INFO

Article history:
Received 25 October 2014
Received in revised form 17 January 2015
Accepted 14 March 2015
Available online 23 March 2015

Keywords:
Simonkolleite
TiO_2
Cr(VI)
Detoxification
Photoreduction
Organic oxidation

ABSTRACT

Innovative simple method for the preparation of simonkolleite-TiO_2 photocatalyst with different Zn contents was achieved. The prepared photocatalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), FT-IR, Raman and diffuse reflectance spectroscopy techniques. The photocatalytic activities of the materials were evaluated for the simultaneous detoxification of hexavalent chromium (Cr(VI)) and oxidation of organic compounds commonly present in wastewater under simulated solar light. The best photoreduction efficiency of Cr(VI) has been achieved at 1000 ppm simonkolleite-TiO_2 photocatalyst of 5% Zn/TiO_2 weight ratio, and pH value of 2.5 to enhance the adsorption onto catalyst surface. Photoreduction was significantly improved by using formic acid as holes scavenger owing to its chemical adsorption on the catalyst surface. Finally, 100% photoreduction of Cr(VI) could be achieved using formic/simonkolleite-TiO_2 systems under sunlight.

1. Introduction

The occurrence of heavy metals in water resources has severe environmental and health impacts. For instance, hexavalent chromium (Cr(VI)) is a significant environmental contaminant because it is highly soluble and highly toxic substance originating from various industrial processes such as electroplating, leather tanning, paint manufacture, pigments, corrosion control and ferrochrome industry (Litter, 1999; Idris et al., 2010; Kebir et al., 2011).The concentration of Cr(VI) in the industrial effluents may reach as much as 200 mg/L (Kebir et al., 2011). It is highly toxic to both plants and animals and it is carcinogenic to humans. Therefore, it is included in the list of priority pollutants by the US Environmental Protection Agency (USEPA) and classified by the International Agency for Research on Cancer (IARC) at the top priority list of toxic pollutants (Lin et al., 2009). Hence, its concentration in drinking water has been regulated in many countries at 0.05 mg/L (Kebir et al., 2011) and this threshold concentration is a challenge for the water quality.

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http://dx.doi.org/10.1016/j.psep.2015.03.010
0957-5820/

Various techniques have been used for the removal of Cr(VI). These techniques include oxidation-reduction, reverse osmosis, electrochemical reduction and ion exchange (Gupta, 2009; Wu et al., 2009; Kebir et al., 2011). Some of these techniques are expensive and inefficient at low concentrations (Kebir et al., 2011). Another removal method is by organic reductant which is considered as an environmental self-cleaning process, particularly for surface water and soil. However, the reduction of Cr(VI) by organic compounds proceeds slowly unless light energy or a catalyst is present in order to accelerate the reaction (Lin et al., 2009).

Heterogeneous photocatalysis is a promising method for water purification and remediation, where organic and inorganic compounds can be degraded or transformed into less harmless substances. To date, titanium dioxide (TiO_2) is one of the most attractive and efficient semiconductor materials suitable for the photoconversion of a wide variety of organic, biological and inorganic substrates that can be either photooxidized or photoreduced in UV irradiated TiO_2 aqueous suspensions. Cr(VI) can be reduced to Cr(III) by TiO_2, where the reduction potential (($E^{o}_{Cr(VI)/Cr(III)}$) = 1.33 V, E shifts 138 mV per pH unit) is more positive than that of the conduction band of the oxide. Most of the literature concerning the photocatalytic reduction of Cr(VI) by TiO_2 was performed using P25 fabricated by Evonik/Degussa (Bickley et al., 1991; Rivera and Hisanaga, 1993; Linsebigler and Yates, 1995; Hoffmann et al., 1995; Tsai, 1997). Recently, TiO_2 and sulphated-TiO_2 powders, prepared by a sol–gel procedure, were employed for promoting the reduction of Cr(VI) (Cappelletti and Ardizzone, 2008). Furthermore, the group of litter (Navio et al., 1998; Navío et al., 1999; Litter, 1999) reported some results on using Fe-doped titania and proposed successive one-electron transfer reducing steps leading to unstable species of Cr(V), which is then reduced to Cr(IV) and to Cr(III), according to equation 1.

$$\mathrm{Cr^{VI}}\xrightarrow{e^-}\mathrm{Cr^{V}}\xrightarrow{e^-}\mathrm{Cr^{IV}}\xrightarrow{e^-}\mathrm{Cr^{III}}\,\frac{1}{2}\mathrm{H_2O}+\mathrm{h^+}\rightarrow\frac{1}{4}\mathrm{O_2}+\mathrm{H^+} \quad (1)$$

Also, titania based materials like, TiO_2 on polystyrene surface and composite TiO_2/acid leached serpentine tailings showed photocatalytic reductive activity for the removal of Cr(VI) (Altın, 2014; Liu and Yin, 2014). Combined process of photocatalysis and adsorption was investigated for simultaneous removal of Cr(VI) and Cr(III) with mixture of TiO_2 and TiO_2 nanotubes (TNTs) (Sun et al., 2013).

However, photoreduction of Cr(VI) is very slow in the absence of hole or $HO^{\bullet}$ scavengers because the anodic pathway, i.e. the oxidation of water by holes, is kinetically sluggish. In the presence of EDTA and other reducing agents, Cr(VI) reduction is greatly accelerated, and hence, the type of the organic compound has significant effect on the photocatalytic reduction process (Litter, 1999). Therefore, photoreduction reaction of Cr(VI) is expected to be favorable in wastewater which are usually contaminated by both organic and inorganic pollutants.

On other hand, interfacial charge-transfer reactions in photocatalyst can be enhanced by doping of the crystalline TiO_2 matrix with other component. For example, Fe^{3+} and Ag^{+}-doped TiO_2 were efficient for oxidation of sucrose to carbon dioxide. $Ti_{1-x}Zr_xO_2$ solid solution exhibited higher photocatalytic activity than pure anatase. Also Mo^{5+}-doped TiO_2 enhanced the photodecomposition of Rhodamine B (Xu et al., 2004).

Simonkolleite ($Zn_5(OH)_8Cl_2{\cdot}H_2O$) was first described by Wang et al. (2005). It occurs as a natural weathering product of Zn-bearing mine slags in the German region of Michelsdorf. The oxygen vacancies on the surface of simonkolleite are electrically and chemically active, as in the case of ZnO. These vacancies may then function as n-type donors and thus significantly increase the material's conductivity (Sithole et al., 2012).

In this work, for the first time, extensive study was done for the preparation of nanocrystalline simonkolleite-TiO_2 photocatalyst by simple co-precipitation method. Development of a suitable technique to detoxify Cr(VI) by reducing it with simultaneous photooxidation of organic substrates under different reaction conditions was also investigated.

2. Experimental

2.1. *Preparation of simonkolleite-TiO_2 photocatalyst*

Titanium tetrachloride ($TiCl_4$), zinc acetate ($Zn(CH_3COO)_2$), methanol (CH_3OH) and ammonia solution (NH_4OH, 33%) were used for the preparation of simonkolleite-TiO_2 photocatalyst. All materials were purchased from Sigma-Aldrich and were used without further purification. Deionized water was used throughout the preparation process.

Ten milliliter of $TiCl_4$ was dissolved in 100 mL C_2H_5OH (solution A). Solution B was prepared by dissolving the desired amount of zinc acetate (0–10% Zn/TiO_2 weight ratio) in 10 mL deionized water. Then, solution A was added drop wisely to solution B under vigorous stirring for 2 h followed by the addition of ammonia solution until pH of solution becomes 7.0. This process was followed by drying the obtained precipitate at 80 °C for few hours. Final produced powder was then washed thoroughly with deionized water in order to get rid of excess chloride ions and later was dried at 105 °C followed by calcination at 450 °C for 2 h. The prepared samples were labeled according to their content of Zn ions, i.e., 1% Zn/TiO_2, 5%/TiO_2 and 10% Zn/TiO_2. The Zn/TiO_2 ratio was measured according to standard methods (Rice et al., 2012) using atomic absorption spectrometer (Varian Spectra 220) with graphite furnace accessory and equipped with deuterium arc background corrector.

2.2. *Characterization of simonkolleite-TiO_2 photocatalyst*

Room-temperature X-ray powder diffraction (XRD) patterns of the prepared samples were collected between 5° and 80° 2θ range using Siemens D5000 diffractometer, using Cu $K\alpha$ radiation. The materials were also characterized by FT-IR spectroscopy using Varian 3100 FT-IR Excalibur Series instrument. Particle size was obtained with the aid of JEOL transmission electron microscope (TEM) (JEM-2010, Japan). The TEM specimens were prepared from a suspension of powder in water. Raman spectra were collected using Bruker RAMIIFT-Raman, with spectral range 3600–70 cm^{-1} Stokes shift, with the resolution of ca. 0.5 cm. Diffuse reflectance measurements were carried out using JASCO spectrophotometer (Model V 570, Japan) equipped with diffuse reflectance accessories, using $BaSO_4$ as the reference sample, within the wavelength range of 200–1000 nm. The absorptions of the samples were plotted in Kubelka–Munk (KM) arbitrary units vs. energy (eV).