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ScienceDirect

Solar Energy 127 (2016) 67–78

SOLAR ENERGY

www.elsevier.com/locate/solener

Solar light mediated photocatalytic degradation of phenol using Ag core – TiO_2 shell ($Ag@TiO_2$) nanoparticles in batch and fluidized bed reactor

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Received 19 October 2015; received in revised form 24 December 2015; accepted 30 December 2015

Communicated by: Associate Editor Gion Calzaferri

Abstract

$Ag@TiO_2$ nanoparticles were synthesised using one pot method followed by calcination at 450 °C for 3 h and were tested for their photocatalytic efficacy in degradation of phenol both in free and immobilized form under solar light irradiation through batch experiments. $Ag@TiO_2$ nanoparticles were found to be effective in solar photocatalytic degradation of phenol. The effect of factors such as pH, initial phenol concentration and catalyst loading on phenol degradation were evaluated and these factors were found to influence the process efficiency. The optimum values of these factors were determined to maximize the phenol degradation. The efficacy of nanoparticles immobilized on cellulose acetate film was inferior to that of free nanoparticles in solar photocatalysis due to light penetration problem and diffusional limitations. The performance of fluidized bed photocatalytic reactor operated under batch with recycle mode for solar photocatalysis of phenol with immobilized $Ag@TiO_2$ nanoparticles was evaluated for large scale application. The performance was found to be dependent on catalyst loading and the optimum is governed by active catalyst sites and light penetration limitations. The photocatalytic degradation of phenol by $Ag@TiO_2$ nanoparticles was only marginally influenced by the presence of small traces of chloride ions. $Ag@TiO_2$ showed a better efficacy as solar photocatalyst than as UV photocatalyst in degradation of phenol. Solar light irradiation is recommended because solar energy, a readily available form of energy can be effectively harnessed for energy efficient, environment friendly and cost effective process. The kinetics of degradation of phenol was found to follow the nth order kinetics with order, $n = 2.19$ for solar photocatalysis.

Keywords: $Ag@TiO_2$; Immobilized nanoparticles; Fluidised bed reactor; Kinetics; Phenol; Solar photocatalysis

1. Introduction

Water pollution is a major cause of concern in most of the countries such as India and other developing nations. Many of the water pollutants are from industrial and municipal wastes and are toxic, persistent and not readily biodegradable. In most of the industries, phenol and phenolic compounds are widely used and have become common pollutants in wastewater bodies. These are released to the environment, from effluents discharged by industries such as petroleum refining, coal tar, pharmaceuticals, pesticides, dyestuff (Lam et al., 2005) synthetic resins, paper and pulp mills, tanning and paint stripping operations and as a byproduct of agricultural chemicals (Parida and

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http://dx.doi.org/10.1016/j.solener.2015.12.049
0038-092X/

Parija, 2006). The phenolic compounds are quite stable and remain in the environment for longer period. Due to their toxicity and carcinogenic character, they are dangerous to the ecosystem in water bodies and human health (Pardeshi and Patil, 2008). According to environment protection rules of Central Pollution Control Board, India (1992) the discharge limit of phenols in inland water is 1 mg/L (Lathasree et al., 2004). Therefore, there is a need of an effective and economic treatment of industrial effluents containing phenolic compounds. Traditional wastewater treatment methods have some limitations and disadvantages. Different treatment methods could be employed for minimizing the concentration of phenols in aqueous solutions. These methods include chlorination (Ge et al., 2008; Sharma et al., 2009), solvent extraction (Egorov et al., 2008; Juang et al., 2008), adsorption (Shawabkeh and Abu-Nameh, 2007) and membrane processes (Lee et al., 2008; Mortaheb et al., 2008; Wu and Li, 2008). These processes are either costly or have the inherent drawbacks of secondary pollution problems (Busca et al., 2008; Patra and Munichandraiah, 2008). Chemical oxidation technique is economically suitable for removal of pollutants of high concentration but cannot mineralize all organics (Takeda and Teranishi, 1988). Biochemical treatment is slow and requires control of proper pH and temperature along with the problem of disposal of activated sludge (Krumme and Boyd, 1988). Alternatively, photocatalytic treatment can be employed to degrade the organics to produce harmless and low-molecular-weight compounds, particularly CO_2 and H_2O.

Heterogeneous photocatalysis was originally used for photoelectrochemical water splitting (Honda and Fujishima, 1972). Photocatalysts such as TiO_2 (Honda and Fujishima, 1972), WO_3 (Sayama et al., 1997; Wang et al., 2000), Fe_2O_3 (Khan and Akikusa, 1999), AgCl (Schürch et al., 2002; Currao et al., 2004a), AgCl combined with Pt and other semiconductors (Schürch et al., 2002), Gold colloid modified AgCl (Currao et al., 2004b), silver nanoparticle modified AgCl (Reddy et al., 2007) have been used for photochemical water splitting (Currao, 2007). Photocatalysis has been further found to be very useful in the abatement of organic and inorganic pollutants (Elsalamony and Abd El-Hafiza, 2014). The use of photocatalysis has been proved to be a good choice to achieve an effective elimination of phenolic compounds. TiO_2 is the most common photocatalyst because of its optical and electronic properties, low cost, chemical stability and nontoxicity (Pelizzetti and Serpone, 1986, 1989; Schiavello, 1988) and proven to be efficient for degradation of phenol (Curcó et al., 1996; Giménez et al., 1999). TiO_2 is known to be an excellent photocatalyst for complete mineralization of phenol in water. Electron–hole recombination leading to lower rate of photocatalysis is a disadvantage of TiO_2 (Liu et al., 2004). Doping metal ions into the TiO_2 lattice has been reported to enhance the photocatalytic efficacy in terms of degradation of dyes (Behnajady et al., 2008; Behnajady and Eskandarloo, 2013a, 2013b), pharmaceutical compounds (Shokri et al., 2013) hexavalent chromium (Eskandarloo et al., 2014) by reduction of electron–hole recombination. Investigations on photocatalysis have been carried out mostly with TiO_2 under ultraviolet light irradiation (Vione et al., 2005). However, sunlight contains only a small fraction (4% of solar energy) of ultra violet light as compared to visible light (43% of solar energy) therefore technological use of TiO_2 is largely impaired (Sakthivel and Kish, 2003). Use of ultraviolet light in bulk level, for the treatment of huge quantity of industrial effluents is not much feasible and economical. In countries where ample amount of sunlight is available, photo catalysis involving sunlight will be economical and preferable. Therefore, there is a need of effective photocatalyst which brings about photocatalytic degradation of organic pollutants under sunlight or visible light irradiation (Pardeshi and Patil, 2008). Nanostructures with Ag core and TiO_2 shell (Ag@TiO_2) can overcome electron–hole recombination limitation and it has been proven to be an efficient photocatalyst under UV and solar light irradiation for degradation of azo dyes (Khanna and Shetty, 2013; Khanna and Shetty, 2014a, 2014b). Ag@TiO_2 has wide application in photocatalysis, as it exhibits photo-induced charge separation, band gap excitation, and charge equilibrium in the Fermi level (Hirakawa and Kamat, 2004). Nanoparticles may be immobilized on suitable support materials (Behnajady et al., 2012) to prevent the difficulties involved in their separation from treated water, possible agglomeration of the nanoparticles and the loss of nanoparticles in continuous flow photocatalytic reactors. Immobilized photocatalysts have been proven to be preferred in continuous photocatalytic reactors (Gadiyar et al., 2013; Behnajady et al., 2011). The main objective of the currently reported research work was to study the photocatalytic efficacy of Ag@TiO_2 nanoparticles in suspended and immobilized form for degradation of phenol in the presence of solar light. To aid in large scale application of immobilized Ag@TiO_2, the performance of fluidised bed reactor operated under batch with recycle mode for solar photocatalysis was studied. Comparison of photocatalytic degradation efficiency of solar photocatalytic process with UV photocatalytic process is reported. The kinetics of degradation of phenol under solar and UV light irradiation using free Ag@TiO_2 nanoparticles are reported.

2. Materials and methods

2.1. Materials

Titanium-(triethanolaminato)isopropoxide ($N((CH_2)_2O)_3TiOCH(CH_3)_2$) (TTEAIP) and Cellulose Acetate were purchased from Sigma–Aldrich Chemicals Pvt. Ltd., Bangalore, India. Phenol (C_6H_5OH) was purchased from NICE Chemicals, Cochin, India. Dimethyl Formamide (DMF), 2-Propanol (GR grade) and silver nitrate ($AgNO_3$)