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Photocatalytic mineralization and degradation kinetics of ampicillin and oxytetracycline antibiotics using graphene sand composite and chitosan supported BiOCl

Bhanu Priya[a], Pooja Shandilya[a], Pankaj Raizada[a], Pankaj Thakur[a], Nahar Singh[b], Pardeep Singh[a,*]

[a] School of Chemistry, Faculty of Basic Sciences, Shoolini University, Solan, Himachal Pradesh, 173212, India
[b] Metrology in Chemistry (ALSIM), CSIR-National Physical Laboratory, Dr K.S. Krishnan Marg, New Delhi, 110012, India

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ABSTRACT

In precedent work, nano-sized BiOCl was immobilized onto graphene sand composite (GSC) and chitosan (CT) to report efficient photocatalytic system for wastewater treatment. GSC was prepared by graphitization of sugar over river sand. The supported BiOCl was prepared by modified hydrolysis method to report BiOCl/GSC and BiOCl/CT photocatalysts. The citric acid directed nucleation and growth process resulted in well dispersed BiOCl nanoplates over GSC and CT. The supported catalysts were characterized by FESEM, TEM, HRTEM, FTIR, XRD, EDX, BET, Raman, photoluminescence and UV–vis diffuse reflectance spectral analysis. The optical band gap of BiOCl/GSC and BiOCl/CT was given by 3.31 and 3.33 eV, respectively. The size of BiOCl/GSC and BiOCl/CT was found to be 50 and 70 nm respectively. The catalytic efficiency of BiOCl/GSC and BiOCl/CT was tested for ampicillin (AMP) and oxytetracycline (OTC) removal. The adsorption of AMP and OTC followed pseudo second order kinetics. Both BiOCl/GSC and BiOCl/CT exhibited significant photocatalytic activity for the mineralization of ampicillin (AMP) and oxytetracycline (OTC) antibiotics under solar light. Simultaneous adsorption and degradation process (A+P) process showed higher antibiotic degradation rate. The applicability of power law model showed the complex nature of mineralization process. During A+P process, both antibiotics were mineralized to CO_2, H_2O and NO_3^- ions. BiOCl/GSC and BiOCl/CT exhibited significant recycle efficiency for 10 catalytic cycles in comparison to native BiOCl.

1. Introduction

The aquatic contamination from the release of antibiotics in water bodies is a major challenge for the environmental engineering around the globe. Ampicillin (AMP) is a semi-synthetic penicillin widely used in human and veterinary medicine. It possesses antimicrobial properties due to presence of β-lactam ring in its structure. Oxytetracycline is one of the detected tetracyclines in water sources and sediments. These antibiotics enter in aqueous system usually from discharge of hospital waste, pharmaceutical manufacture, livestock and agriculture. Their presence exerts unfavorable effects on aquatic systems, not only resulting in the development of a variety of resistant bacteria but also disturbing the aquatic animal life [1,2]. Nowadays, various physico-chemical methods such as membrane separation, chemical oxidation, adsorption, coagulation, flocculation, ozone treatment, reverse osmosis and filtration have been used to eliminate antibiotics form aquatic environment. However, these methods either fail to attain complete breakdown of antibiotic or produce large volume of toxic sludge which results in disposal problem [3]. Therefore, more competent treatment techniques are needed for complete elimination of antibiotics form wastewater.

From the aforesaid perspective, solar light assisted photocatalysis is emerging as a green technology for waste water treatment [3]. Since the exploration of photocatalytic activity of TiO_2, it is being used in laboratories and industries for significant photocatalytic activity [4]. However its wide band gap and rapid recombination of photo-generated electron holes-pair limits its applications under solar light which contains only 5% of UV light [5]. In order to exploit 52% visible light of solar spectrum, visible light active photocatalyst is highly needed for photocatalysis properties [6]. Although variety of narrow-band gap semiconductor photocatalyst such as

* Corresponding author.
E-mail address: pardeepchem@gmail.com (P. Singh).

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Ag_3PO_4, CdS, Cu_2O, ZnS and PbS possess high visible light activity. However, instability in aqueous medium and toxicity put thrust on the development of more robust photocatalytic system for water purification [7].

During last decade, BiOCl has gained more and more attention as a promising photocatalyst for photocatalytic energy conversion and environmental remediation [8]. The layered structure of BiOCl endows it with fascinating physicochemical properties, suitable band gap, non-toxicity, high chemical and corrosion resistance [9]. The positive conduction band and layered structure (Cl-Bi-O-Bi-Cl) along 'c' axis enable easier separation of photo generated electron and hole pairs. In last decades several nanostructures like nanowires, nanoplates, nanofibers, nanobelts, nanoflakes, nanospheres, 2D, 3D hierarchical structures have been synthesized by hydrothermal, solvothermal, ionothermal routes [10]. However sheet like structure has been obtained mainly by hydrolysis method using Bi^{3+}-Cl^- aqueous system [11]. The use of capping agent has proven an effective mean to control the activity of cations and retarding the grain growth of inorganic semiconductors [12]. Citric acid is a non-toxic and stable organic compound that has been proven as a good capping agent for the complexation with Bi^{3+}, Al^{3+}, Ca^{2+}, Fe^{3+}, $Zn^{2+}$and Mn^{2+} ions [13]. Xiong et al. prepared mannitol assisted well crystalline square like plate structure for effective photo degradation of rhodamine B dye [14]. Song el al. synthesized hierarchical BiOCl crystals via pyridine mediated solvothermal routes [15].

From application prospective, the main drawbacks of nano-sized inorganic nanoparticles are complex filtration processes and highly turbid solution that decrease the photoactive surface area during photodegradation process [16]. Secondly, preliminary adsorption of aqueous phase pollutants is required for efficient surface photodegradation reactions [17]. These concerns have motivated researchers to develop supported photocatalytic systems in which nano-sized BiOCl nanoparticles can be immobilized on different supports. The support should have long term stability, capability to delocalize electrons and endure the oxidative radical attack during exposure to light [18]. As the most recently discovered carbonaceous material, graphene and its derivatives have attracted remarkable attention due to high surface area and electron mobility. Graphene is a single layer sp^2 hybridized carbon organized in honeycomb structure [19,20]. Fu et al. synthesized magnetically separable $ZnFe_2O_4$/graphene nanocomposite which exhibited dual functions as a photo electrochemical degrader and an OH&903; generator *via* photo electrochemical decomposition of H_2O_2 [21]. Hu et al. prepared graphene supported ZnS nanocomposite using microwave radiation assisted method [22]. Liu et al. synthesized BiOI/GR composite through hydrothermal method and claimed their improved photocatalytic activity and stability for methylene green dye degradation [23]. In recent time, chitosan, a non-toxic, biocompatible and abundant biopolymer has emerged as an absorbent for heavy metals, organic and inorganic pollutants [24]. Chitosan possesses amine(-NH_2) and hydroxyl (-OH) groups in water that can serve as reaction sites for immobilization of inorganic nanoparticles and adsorption of aqueous phase contaminant [25]. Farzana et al. synthesized zinc impregnated chitosan beads for the removal of methylene blue and rhodamine B dye [25].

This research was focused on the preparation of GSC and CT supported BiOCl nano composites using simple hydrolysis method. GSC was prepared form highly carbonaceous material sucrose which is non-toxic to human and environment [26]. Both BiOCl/GSC and BiOCl/CT were characterized using FESEM TEM, HRTEM, BET, XRD, EDX, Raman, photo luminescence and UV–vis analysis. The photocatalytic performance of BiOCl/GSC and BiOCl/CT was tested for the complete mineralization of AMP and OTC antibiotics. The effect of adsorption on photocatalytic antibiotic degradation was also investigated. More specifically, the co-operative effect between adsorption and photocatalysis was explored to optimize the degradation rate. The power law model was applied to understand the intricacies of long term mineralization process. The recycle efficiency of BiOCl/GSC and BiOCl was also evaluated for ten cycles to ensure the applicability of BiOCl/GSC and BiOCl/CT as effective photocatalysts.

2. Experimental

2.1. Preparation of graphene sand composite (GSC)

In this work, GSC was prepared with modification in earlier reported method [27]. The common sugar cubes was used as the carbon source for the preparation of GSC. 1.0 g of sugar cubes were dissolved in water to obtain a homogenous solution. To this solution, 0.5 g of sand was added and mixture was stirred for 7 h to get slurry. The obtained mixture was dried at 90 °C to obtain sugar-coated sand. The sugar-coated sand was heated at 750 °C for 3 h to ensure the graphitization of sugar molecules. The obtained material was allowed to cool at room temperature and the resultant black sample was leveled as GSC.

2.2. Synthesis of BiOCl/GSC and BiOCl/CT

BiOCl/GSC was prepared using modified hydrolysis method [13]. Typically, 1 g of $BiCl_3$ was dissolved in 80 mL of distilled water. To this solution 20 mL of concentrated hydrochloric acid was added and mixture was stirred to obtain a transparent $BiCl_3$-HCl aqueous solution. Subsequently, 20 mL of citric acid (1.0×10^{-3} mol/L) was added to reaction mixture. To this solution 0.2 g of GSC was added. The reaction mixture was heated at 60 °C with continuous stirring for 3 h to obtain precipitates of BiOCl/GSC. The precipitates were washed with distilled water and then dried at 90 °C. The BiOCl/GSC was preserved for further use. BiOCl/CT was prepared using same methodology with addition of CT in place of GSC. BiOCl/CT precipitates were dried at 50 °C to prevent the decomposition of chitosan. During synthesis of BiOCl, neither GSC nor CT was added to reaction mixture.

Field emission scanning electron analysis was carried using model Nava Nano SEM-45(USA). Sample surfaces were observed at different magnification and images were recorded. HRTEM and Energy dispersive X-ray analysis was performed at randomLy selected areas under vacuum conditions using model FP/5022–Tecnai G2 20 S-TWIN (USA). Fourier- transform infrared (FTIR) analysis was performed using Perkin – Elmer Spectrometer (Spectrum RX-I). Panalytical's X'Pert Pro-diffractrometer having Cu K-α-1 radiation source along with beta filter made of nickel metal was used for XRD pattern. The optical absorption performance of catalysts was estimated by using a diffuse reflectance spectrophotometer (UV 3600, Shimadzu) using $BaSO_4$ as reference. The specific surface area of samples was estimated by nitrogen adsorption–desorption isotherms according to Brunauer–Emmett–Teller analysis (Autosorb I; Quatachrome Corp.). The photoluminescence emission analysis was performed using inductively coupled plasma-optical emission spectrometer (ICP-OES), Thermo-iCAP 6000 Series model to find the very low concentration of elements.

2.3. Photocatalytic and adsorption experiments

The adsorption and photocatalytic activity of BiOCl/GSC, BiOCl/CT and pure BiOCl was evaluated using double walled pyrex cylinder surrounded by thermostatic water circulation arrangement (30 ± 5 °C) (Supplementary Fig. S1). The suspension containing antibiotics and photocatalyst was kept under solar light with continuous stirring. The aliquot (3 mL) was withdrawn