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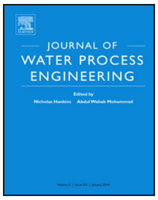

Solar photocatalytic mineralization of antibiotics using magnetically separable $NiFe_2O_4$ supported onto graphene sand composite and bentonite

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ABSTRACT

Adsorbent supported photocatalysis is developing as a potential waste water treatment technology. In this work, $NiFe_2O_4$ was supported onto graphene sand composite (GSC) and bentonite (BT) supported to prepare magnetic $NiFe_2O_4$/GSC and $NiFe_2O_4$/BT nanocomposties. Graphene sand composite (GSC) was prepared by graphitization of sugar over river sand. The size of $NiFe_2O_4$/BT and $NiFe_2O_4$/GSC was found to be 50 and 60 nm respectively. Mesoporous nature of prepared photocatalysts was confirmed by BET adsorption/desorption experiments. $NiFe_2O_4$/GSC and $NiFe_2O_4$/BT exhibited ferromagnetic behaviour and could be separated from treated water using external magnetic field. The band gaps of $NiFe_2O_4$/GSC and $NiFe_2O_4$/BT were found to be 2.41 and 2.42 eV, respectively. The adsorption and photocatalytic activity of $NiFe_2O_4$/GSC and $NiFe_2O_4$/BT was tested for the mineralization of ampicillin (AMP) and oxytetracycline (OTC) antibiotics under solar light. The adsorption process had significant effect on the mineralization of AMP and OTC. Simultaneous adsorption and degradation (A + P) process were the most efficient for antibiotic degradation. The complete mineralization of antibiotics was obtained using $NiFe_2O_4$/GSC/A + P and $NiFe_2O_4$/BT/A + P catalytic processes. The kinetics of mineralization were explored using power law model. Magnetically recoverable $NiFe_2O_4$/GSC and $NiFe_2O_4$/BT are recyclable and displayed significant recycle efficiency and quick recovery for 10 consecutive catalytic cycles.

1. Introduction

From an environmental researcher point of view, pharmaceuticals including antibiotics are a new group of man-made chemicals entering into aquatic environment [1,2]. Antibiotic is one of the worldwide used pharmaceuticals that are found to be toxic to the ecosystem [3–5]. Antibiotics are the hazardous contaminant which find their way into various water sources from sewages of pharmaceuticals industries, hospitals and other medical facility. The major problem emerges due to the presence of antibiotic in an aqueous system is the development of an antibiotic resistant bacteria [6]. Ampicillin is semi-synthetic penicillin retrieving their antimicrobial property from the beta-lactam ring [7]. Oxytetracycline (OTC) is one of the most often detected tetracyclines in water bodies [8,9]. In the regard of above-mentioned issue, several conventional methods such as membrane separation, chemical oxidation, adsorption, coagulation, flocculation, treatment with ozone, reverse osmosis and filtration have been used to evacuate antibiotics form aqueous system [10]. These antibiotics are difficult to remove by conventional methods due to their antibiotic nature, hydrophilicity and stable ring structure which may threaten the quality of drinking water [11]. Therefore, more competent treatment techniques are needed for complete removal of antibiotics. From this perspective, solar light assisted photocatalysis is emerging as a green technology for waste water treatment. Among several engineered nanomaterials, TiO_2 based photocatalytic systems have been exhaustively researched and used in laboratories and in industries with significant photocatalytic activity [12]. The wide band gap photocatalyst absorb photons only in UV range with limited photocatalytic activity under solar light as it comprises of only 5% of UV light. Although many visible light responsive photocatalyst such as Ag_3PO_4, CdS, Cu_2O, ZnS, PbTe and PbS, $TiO_{(2\text{-}x)}N_x$,$BiVO_4$, Ag/AgCl, $InMO_4$ (M = Nb, Ta) etc. have been extensively studied for wastewater treatment

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[12–17]. The separation of inorganic photocatalyst from treated water, especially form large volume of water is very difficult and expensive. Sedimentation and centrifugation process are difficult to employ at large scale because of long time duration and technical limitations [18,19]. In this respect, magnetic spinel structured ferrite nanoparticles has been intensively investigated due to their unique physical and chemical properties as well as their various applications [20].

Among various magnetic oxide, spinel ferrites, MFe_2O_4 (M = Ni, Co, Zn, Ni, Mg etc.) are well-known for cubic spinel materials where oxygen atom possesses a face centered cubic (fcc) close packing and M^{2+}, and Fe^{3+} occupy either tetrahedral or octahedral interstitial sites [21,22]. Particularly $NiFe_2O_4$ is an inverse spinel in which equal number of Ni^{2+} and Fe^{3+} resides on octahedral sites and remaining Fe^{3+} resides on tetrahedral sites. The optical band gap of $NiFe_2O_4$ is 2.19 eV [23]. Nickel ferrite ($NiFe_2O_4$) with good magnetism has been widely used in water purification technology. Ren et al. synthesized magnetic $NiFe_2O_4/Bi_2O_3$ heterostructure via microwave assisted hydrothermal method and explored their photocatalytic activity for antibiotic degradation in an aqueous system [24]. Fu et al. prepared magnetically separable graphene supported $NiFe_2O_4$ and noticed highly active photocatalyst for the degradation of methylene blue (MB) under visible light [25]. Jin et al. reported magnetic $TiO_2/SiO_2/NiFe_2O_4$ composite and investigated their photocatalytic activity for the degradation of basic violet (BV5) under UV radiation [26]. However, small size, magnetic interaction and agglomeration of nanosized ferrites make difficult recovery of photocatalyst during large scale water purification process. Moreover, preliminary adsorption of aqueous phase pollutant is also required for efficient photodegradation reactions occurring on the photocatalyst surface [27]. The immobilization of nano-sized metal oxide particles onto appropriate support materials emerge as better supported photocatalytic systems. The support materials should have long term stability and endure the oxidative radical attack during exposure to light. As carbonaceous material, graphene and its derivatives have attracted tremendous attention due to high surface area and electron mobility. Graphene is a single layer sp^2 hybridized carbon organized in honeycomb structure [28]. Graphene is considered a potential candidate for the fabrication of graphene supported nanocomposite photocatalyst. Hu et al. prepared graphene supported ZnS nanocomposite using microwave radiation assisted method [29]. Liu et al. synthesized BiOI/graphene composite through hydrothermal method and claimed their improved photocatalytic activity and stability for methylene green dye degradation [30].

Due to low cost, abundant availability and environmental friendly nature, bentonite clay is an attractive support for all kinds of photocatalysts. It is phyllosilicate mineral having stacked layers (2:1) with two tetrahedral sheets sandwiching an octahedral sheet and possessing a swelling behaviour. Bentonite has a permanent negative charge due to the isomorphous substitution ofAl^{3+} for Si^{4+}in the tetrahedral site and Mg^{2+} for Al^{3+} in the octahedral site [31]. Bentonite has excellent adsorption/ion exchange site for metal ions and organic pollutants within its interlayer space. Many studies have revealed that bentonite is emerging as a good support for the preparation of composite photocatalysts with significant photocatalytic activity. For instance, ZnS/bentonite [32], TiO_2/bentonite [33], CdS/bentonite [34], g-C_3N_4/bentonite [35], MoS_2/bentonite [36] etc. were previously synthesized and tested for their improved photocatalytic activity.

In precedent work, $NiFe_2O_4$ was dispersed over graphene sand composite and bentonite to obtain $NiFe_2O_4$/GSC and $NiFe_2O_4$/BT photocatalyst using solvothermal method. Graphene sand composite was prepared form sucrose which is a non-toxic and highly carbonaceous material [37]. The river sand was used as inexpensive support to make liquid-solid separation easier. Graphene and graphene oxide were anchored onto river sand resulted in higher adsorption of organic phase pollutants [37]. The photocatalytic activity of $NiFe_2O_4$/GSC and $NiFe_2O_4$/BT was explored for the mineralization of ampicillin and oxytrertacyline antibiotics. Power law model was applied to understand kinetics of long term mineralization process. The recycle efficiency of $NiFe_2O_4$/GSC and $NiFe_2O_4$/BT was also examined for ten cycles to ensure the stability of photocatalyst during photodegradation process.

2. Experimental

2.1. Synthesis of graphene sand composite (GSC)

Graphene sand composite was prepared with modification in previously reported method [37]. The common sugar was used as the carbon source for the preparation of GSC. Typically, 1 g of sugar was dissolved in 100 ml of water to obtain homogenous solution. To this mixture, 0.5 g of river sand and mixture was stirred for 7 h to get thick slurry. The obtained mixture was dried at 90 °C in hot air oven to obtain sugar-coated sand. The sugar-coated sand was heated at 750 °C for 3 h to achieve complete graphitization of sugar molecules. The obtained sample was allowed to cool at room temperature to obtain GSC. The obtained black sample was labled as graphene sand composite (GSC). Bentonite was procured from Sigma Aldrich India and used without further purification.

2.2. Preparation of $NiFe_2O_4$/BT and $NiFe_2O_4$/GSC

$NiFe_2O_4$/BT and $NiFe_2O_4$/GSC composite were synthesized *via* modified solvothermal method [38]. Briefly, 0.2 M (25 ml) of $NiCl_2{\cdot}6H_2O$ and 0.4 M (25 ml) $FeCl_3{\cdot}6H_2O$ solution were prepared in double distilled water and two solution were mixed with constant stirring for 30 min. To above solution, 1.0 g of bentonite was added and sonicated with ultrasonic waves of 20 kHz intensity for 15 min. The pH of the reaction mixture was adjusted to 10. The mixture was heated at 80 °C for 3 h to obtain $NiFe_2O_4$/BT. The precipitates were filtered and washed with double distilled water and ethanol. The obtained sample was dried in vacuum oven at 70 °C for 3 h. $NiFe_2O_4$/GSC was also prepared by using same methodology as mentioned above.

Both $NiFe_2O_4$/GSC and $NiFe_2O_4$/BT were characterized using FESEM, TEM, XRD, FTIR, BET, FT-Raman, VSM, EDX and UV–vis diffuse reflectance analysis. FESEM micrographs of prepared samples were obtained through model Nava Nano SEM-45(USA). Sample surfaces were then observed at different magnification and images were received. HR-TEM 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 Spectra (FTIR) was obtained using Perkin–Elmer Spectrometer (Spectrum RX-I). Panalytical'sX'Pert Pro diffractrometer was used for powder XRD. The radiations used are Cu K-α-1 where a nickel metal is used as beta filter for identification of various phases and crystalinity. The optical absorption performance of catalysts was estimated by using a diffuse reflectance spectrophotometer (UV 3600, Shimadzu) using $BaSO_4$ as reference. The magnetic studies were carried out using vibrating sample magnetometer (Cryogenic). Raman spectra were obtained using FT-Raman spectrometer (BRUKEF RFS 27: standalone with range of 50–4000 cm^{-1} using 2 cm^{-1} resolutions). The specific surface area of adsorbent was measured by nitrogen adsorption–desorption isotherms according to the Brunauer–Emmett–Teller analysis (Autosorb I; Quatachrome Corp.).

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