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Degradation of methylene blue and congo-red dyes using Fenton, photo-Fenton, sono-Fenton, and sonophoto-Fenton methods in the presence of iron (II,III) oxide/zinc oxide/graphene (Fe_3O_4/ZnO/graphene) composites

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ABSTRACT

In a quest to develop effective methods for the elimination of organic pollutants and water remediation, a series of Fe_3O_4/ZnO/graphene composites are prepared and characterized. These composites are utilized as heterogeneous catalysts during the Fenton oxidation reaction for the degradation of the dyes, Congo red (CR) and methylene blue (MB), in aqueous solutions in the dark or under light and ultrasound, separately or simultaneously. The effects of various parameters, such as initial pH, H_2O_2 concentration, and graphene content, on the activity of the catalysts and, the iron leaching from the heterogeneous catalyst are investigated. The results demonstrate that all the catalysts exhibit excellent activities during the Fenton reaction under light and ultrasonic irradiation and that the incorporation of graphene significantly accelerates the MB and CR degradation. Complete elimination of CR and MB can be achieved in less than 1 h by simultaneous light and ultrasonic irradiation although CR was more effectively degraded as compared to MB. Moreover, the incorporation of graphene could reduce the leaching of iron ions from Fe_3O_4 to the solution. Thus, the Fe_3O_4/ZnO/graphene composite exhibits good stability after 4 repetitions of the cycling process.

1. Introduction

Wastewater effluent from industries using dyes and pigments contains high concentration of organics which exhibits a devastating impact on aquatic ecosystems and the health of human beings [1,2]. Following the report by Henry. J. H. Fenton in 1894 about the capability of H_2O_2 to oxidize tartaric acid in the presence of Fe(II) salts [3], the Fenton reaction was developed; several decades later, it has become extensively used for the elimination of organic pollutants. Briefly, the dissolution of iron ion in the waste water solution, to which hydrogen peroxide is added, promotes the generation of oxidative hydroxyl radicals ($^{\cdot}OH$), which efficiently decompose the organic pollutant [4,5]. However, the homogeneous Fenton reaction still presents several limitations; for instance, (1) high rate leaching of iron ions and could only be activated under acidic condition. In this regard, the heterogeneous Fenton reaction has been reported to limit iron leaching and to extend the pH activation conditions [6,7]. Over the previous decade, the heterogeneous Fenton reaction based on magnetite nanoparticles has been demonstrated as an effective tool to eliminate organic pollutants and water remediation taking advantage of the presence of the octahedral sites in such nanoparticles, which can accommodate both Fe^{2+} and Fe^{3+} ions [8,9]. In this reaction, iron ions (Fe^{2+}) react with hydrogen peroxide to generate $^{\cdot}OH$, which are responsible for the oxidation of organic compounds [9].

Several studies have showed that external irradiation such as light and ultrasound irradiation can enhance the efficiency of the Fenton reaction by increasing the degradation rate via regeneration of the Fe^{2+} ions [10–12]. Using light irradiation in the Fenton system (photo-Fenton) the degradation of organic pollutants could be accelerated owing to the ability of light to reduce Fe^{3+} into Fe^{2+} ions [10]. Ultrasound-supported Fenton reaction (sono-Fenton) also could improve the degradation of organic pollutants by creating additional $^{\cdot}OH$ through cavitation and also accelerate the regeneration of Fe^{2+} [13,14]. Moreover, a combination of UV or visible light irradiation with ultrasound irradiation in the Fenton reaction became a promising method because of the synergistic effect between UV or visible light irradiation and ultrasound irradiation. The application of ultrasound and UV or visible light in catalytic reactions not only creates effective radicals required for degradation but also continuously cleans the surface of catalysts to avoid the accumulation of pollutants and their

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intermediates produced during degradation. Furthermore, this application enhances the surface area of the catalyst together with promoting the mass transfer of organic pollutants between the liquid phase and the catalyst surface [15].

Introducing a metal oxide semiconductor to the Fenton system expands the operating pH range and also reduces the problem that is associated with leaching; this further enhances the performance of the system during the degradation of the organic pollutant [16]. Due to their electronic structure, metal oxide semiconductors can act as sensitizers in light-induced redox processes and can also act as photocatalysts that support the degradation of organic pollutants [17]. Among the metal oxide semiconductors, zinc oxide is one of the most promising materials because it exhibits relatively high photocatalytic activities. In addition, it also exhibits excellent thermal, biological, and chemical stabilities and long lifespans, while being non-toxic and inexpensive [18,19]. However, key drawbacks of zinc oxide are the fast recombination of photo-generated electrons and holes and the fact that its photocatalytic activity is limited to irradiation in the ultraviolet (UV) light region [20–22]. With the aim at extending the applicability of the UV-Fenton reaction into the visible light, several methods have been explored, including the development of a support medium for the heterogeneous Fenton catalyst.

In this context, graphene, a single layer material covalently organized in two-dimensional lattices of sp^2-bonded carbon atoms, offers a promising approach due to its strong adsorption ability [23,24]. As a support medium, graphene can not only transfer electrons but also enhance visible-light response [25]. In addition, graphene has been used as supported adsorbent for removal of organic pollutants [26]. Stemming from these considerations, an enhancement of the heterogeneous Fenton process can be expected from the combination of the advantages of graphene with the strong adsorption ability and physicochemical stability of Fe_3O_4/ZnO nanocomposites.

In this study, the use of Fe_3O_4/ZnO/graphene nanocomposites as Fenton catalysts is proposed for the removal of both cationic (methylene blue, MB) and anionic (Congo red, CR) dyes from aqueous solutions in a wide pH range (3–13), not only in the adsorption process alone but also under simultaneous light and ultrasonic irradiation. In particular, the influence of some key operating parameters such as graphene loading, initial pH, H_2O_2 concentration, and reaction temperature was investigated. To gain more insight into the process, the reaction mechanism was explored and correlated with the physical properties of the catalyst, whose stability was also evaluated.

2. Materials and methods

2.1. Materials

Iron (II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, 99%), zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$, 99%), sodium hydroxide (NaOH), benzoquinone ($C_6H_4O_2$), *tert*-butanol ($C_4H_{10}O$), sodium sulfate (Na_2SO_4), ammonium oxalate ($C_2H_8N_2O_4$), hydrogen peroxide (H_2O_2 30%), ethanol, and ethylene glycol ($C_2H_6O_2$) were purchased from Merck and used without further purification. Graphene (N002-PDE) was purchased from Angstron Materials.

2.2. Synthesis of Fe_3O_4/ZnO/graphene nanocomposites

Fe_3O_4/ZnO/graphene nanocomposites were obtained using sol–gel method followed by hydrothermal method. Thus, the preparation of the Fe_3O_4/ZnO nanocomposites was performed using the sol–gel method previously reported [27], and their incorporation with graphene was performed using a simple hydrothermal method. Briefly, 20 mg of graphene was dissolved in a solution of water (80 mL) and ethanol (40 mL) through ultrasonic treatment for 2 h, followed by the addition of 2 g of Fe_3O_4/ZnO and stirring for 2 h to achieve a homogeneous suspension. The suspension was then put into a 200 mL Teflon-sealed autoclave and maintained at 120 °C for 3 h. The resulting nanocomposite was isolated by centrifugation and dried at 70 °C for 12 h. The Fe_3O_4/ZnO/graphene nanocomposites were obtained with graphene contents of 1 wt% and 3 wt% and were labeled as F3Z-1G and F3Z-3G, respectively.

2.3. Characterization techniques

The crystallite structure of the catalysts was characterized via X-ray diffraction (XRD, Rigaku MiniFlex 600) and Fourier transform infrared spectroscopy (FT-IR, Shimadzu IR Prestige 21). Raman spectra were acquired on a Raman microscope (Thermo Scientific DXR *xi Raman* Imaging *Microscope*) with a 5 mW 532 nm laser as the monochromatic radiation source. In addition, elemental analyses and the morphologies of the samples were determined using energy dispersive X-ray (EDX) spectroscopy (LEO 420) and transmission electron microscopy (TEM, FEI Tecnai G2 SuperTwin). X-ray photoelectron spectroscopy (XPS) was conducted on a PHI-5400 instrument (Physical Electronics) with an Al-Kα (1486.6 eV) X-ray source. The nitrogen ad/desorption isotherms were measured using a Quantachrome Nova 2000 instrument. The total surface area and pore size distribution were determined via the BET and BJH methods, respectively. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM, Oxford type 1.2T). Thermogravimetric analysis (TGA) of the adsorbent was conducted using a Rigaku TG8121 device. The adsorbents were heated from room temperature up to 1000 °C at a rate of 2 °C/min. A flow of argon was maintained during the analyses.

2.4. Fenton process

The obtained Fe_3O_4/ZnO/graphene nanocomposites were used as Fenton catalysts for the removal of MB and CR in the presence of H_2O_2. All Fenton experiments were conducted in batch mode in a thermostatic water bath. Before the Fenton reaction was conducted, the pH of the dye solution was adjusted from 3 to 13 by adding NaOH or CH_3COOH. Fenton catalysts were added into the dye solution, where the initial concentration of dye was 40 mg/L. Fenton experiments were carried out at constant pH and temperature. The reaction was initiated by adding 4 mL of H_2O_2 in the dye solution. Once H_2O_2 was added, the Fenton reaction of dye started. In order to measure the quantity of dye removed as a function of time interval, the catalyst was separated from the solution using an external magnetic field.

2.5. Photo-Fenton, sono-Fenton, and sonophoto-Fenton processes

For the evaluation of the photo-Fenton activities of the Fe_3O_4/ZnO/graphene nanocomposites, the reactions were conducted in a cylindrical glass vessel equipped with a magnetic stirrer, in which two 40-W UV-C lamps and a 40-W Xe lamp with an intensity of around 50,000 Lux were used as light sources. In the sono-Fenton process, an ultrasonic bath operated at fixed frequency and power of 40 kHz and 150 W, respectively, was used as ultrasound source. The ultrasound (US) or/and UV/visible sources (US + UV/Vis) were then turned on, and the analysis process was analyzed after light or ultrasound were applied. Under ambient conditions and stirring, the contents of the glass vessel were alternately exposed to UV/Vis, US, and US + UV/Vis irradiation at regular intervals for 2 h.

3. Results and discussion

3.1. Characteristics of the Fe_3O_4/ZnO/graphene nanocomposites

The XRD patterns of the Fe_3O_4/ZnO/graphene nanocomposites for various graphene contents are depicted in Fig. 1a. The XRD peaks from Fe_3O_4, ZnO, and graphene are also plotted in the figure for comparison. The diffraction patterns for the Fe_3O_4/ZnO/graphene nanocomposites