



Heterogeneous sono-Fenton-like process using magnetic cobalt ferrite-reduced graphene oxide (CoFe₂O₄-rGO) nanocomposite for the removal of organic dyes from aqueous solution

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ARTICLE INFO

Keywords:

Cobalt ferrite
Reduced graphene oxide
Nanocomposites
Heterogeneous sono-Fenton-like
Sonocatalytic removal
Organic dyes

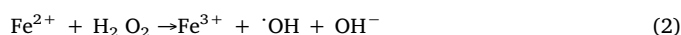
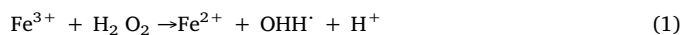
ABSTRACT

We report herein the synthesis of monodisperse cobalt ferrite (CoFe₂O₄) nanoparticles (NPs) via a surfactant-assisted high temperature thermal decomposition method and then their assembly on reduced graphene oxide (rGO) to yield CoFe₂O₄-rGO nanocomposites, which displayed outstanding sonocatalytic activity for the removal of organic dyes from aqueous solutions under ultrasonic irradiation. As-prepared CoFe₂O₄-rGO nanocomposites were characterized by using transmission electron microscopy (TEM), high-resolution scanning electron microscopy (HR-SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Micro-Raman spectroscopy, Vibrating sample magnetometer (VSM) and inductively couple plasma mass spectrometer (ICP-MS). To evaluate the sonocatalytic activity of the CoFe₂O₄-rGO nanocomposites, the sonocatalytic removal of several organic dyes (AO7, AR17, BR46 and BY28) was studied. The reaction conditions were optimized by studying the effects of various key operating parameters such as pH, catalyst dosage, H₂O₂ initial concentration, initial dye concentration, ultrasonic power and reaction time on the removal of AO7 dye. The maximum removal efficiency of 90.5% was achieved at pH 3 using 0.08 g L⁻¹ catalyst, 3 mM H₂O₂ and 10 mg L⁻¹ AO7 dye under 350 W ultrasonic power in 120 min of reaction time span. Experimental results revealed that the kinetic of the removal process could be described using Langmuir-Hinshelwood (L-H) kinetic model. The trapping experiments showed that O₂^{•-} radicals constitute the major reactive oxygen species (ROS) in the AO7 dye removal process. The reusability of the nanocomposites revealed about 22% drop in the removal efficiency within five consecutive runs. A possible sonocatalytic mechanism for the removal of organic dyes was also proposed. The intermediate by-products of the dye formed in the removal process were characterized by using the GC-MS technique.

1. Introduction

Many manufacturing industries, especially textile industry, produce colored effluents that entail serious hazards for the water resources [1,2]. The discharge of synthetic wastewater into water bodies initiates hazardous chemical processes due to richness of color and lower biodegradability compared to other substances [3,4]. A sustainable healthy environmental requires elimination of such contaminating organic substances from the water sources [5]. Great efforts are currently concentrated by researchers on developing efficient solutions to remove such toxic chemicals [6–8]. The widespread use of Advanced Oxidation Processes (AOPs) throughout the past decades has caused the studies to focus on treatment of organic pollutants of toxic and refractory nature owing to the unique advantages of AOPs [9,10]. The ultrasonic and Fenton processes among AOPs are considerably convenient and efficient green treatment technologies extensively applied for the

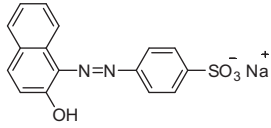
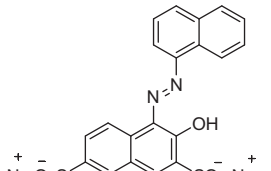
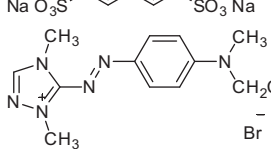
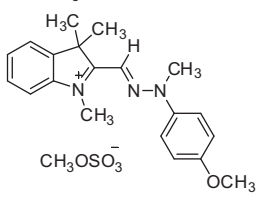
elimination of numerous polluting agents of effluents [11]. As the key component in AOPs, the hydroxyl radicals (•OH) unselectively attack the organic pollutants and ultimately convert them into carbon dioxide, water and inorganic salts [12]. Heterogeneous Fenton-like process form •OH radicals; in such processes the Fe³⁺ ions are used as Fe²⁺ source (Eqs. (1) and (2)). They can also be obtained through water cleavage by ultrasonic waves (Eq. (3)) as the result of cavitation phenomenon [11]. Studies have shown that the hydrogen peroxide (H₂O₂) can be released in the solution under the effect of ultrasonic irradiation (Eq. (4)) [9,13].



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Table 1
Chemical structures and characteristics of organic dyes.

Dye	Chemical structure	Molecular formula	Mw (g mol ⁻¹)	$\lambda_{\max}$ (nm)	Chemical class
AO7		C ₁₆ H ₁₁ N ₂ NaO ₄ S	350.32	484	Monoazo
AR17		C ₂₀ H ₁₂ N ₂ Na ₂ O ₇ S ₂	502.42	522	Monoazo
BR46		C ₁₈ H ₂₃ BrN ₆	403.32	531	Monoazo
BY28		C ₂₁ H ₂₇ N ₃ O ₅ S	433.52	439	Azomethine

When the ultrasonic waves enters into a liquid medium, the cavitation phenomenon causes the formation, growth, and collapse of microbubbles that produce localized high temperatures as well as pressure based on the hot spot approach [14,15]. However, the application of ultrasonic waves to remove organic colorful pollutants needs a prolonged reaction process and thus has limited applicability [16]. To solve this limitation, the technique is incorporated with complementary methods such as the Fenton-like systems through application of a catalyst which is usually iron-based [11]. However, this method has also several drawbacks including pH controlled to avoid the accumulation of Fe³⁺ and the catalyst separation from the effluent. To eliminate these drawbacks, the Fenton process is employed through the application of heterogeneous catalysts [17,18]. Recently the magnetic nanoparticles (MNPs) utilization in heterogeneous Fenton system has been the central focus of researchers for the potential that external magnetic fields (ferromagnetism) can provide for separation of catalyst from the system [19,20]. This technique has been approved for its rapid and efficient performance for separation of magnetic particles from the multi-component compositions [19].

CoFe₂O₄ nanocrystals with their spinel structure and unique properties (e.g. high saturation magnetization, low cost, and size- and shape-dependent magnetic behavior) have turned out to be useful material for environmental remediation [19,21]. Graphene, a two-dimensional form of carbon, also has unique physical, chemical and mechanical properties, opening up new research area of condensed-matter physics to find wide-ranging and diversified pro-environmental applications [22]. Such wonderful properties have enabled the researchers to use it as support for catalysts. Another promising technique for removal of pollutants from colorful wastewater is the dispersion of MNPs on graphene sheets [23,24]. Following this objective, a number of recent studies have reported the use of graphene-based hybrids containing MNPs [19,23,25]. Advantages such as the low cost, the possibility of waste reuse and the optimal adsorption capacity of rGO, as well as the high sonocatalytic activity of CoFe₂O₄ can help the new nanocomposites to develop a new method which would be economical, nontoxic and effective for removing organic pollutants from the aqueous

medium. To the best authors' knowledge, this study is the first example addressing for the preparation of ex-situ controlled assembly of CoFe₂O₄ NPs on rGO to yield CoFe₂O₄-rGO nanocomposites and the application of the resultant nanocomposites in the sonocatalytic removal of dyes.

With the scope described above, the main goal of this study was investigating the utilization of CoFe₂O₄-rGO nanocomposites for the sonocatalytic removal of organic dyes from aqueous solution. In this study, a number of experimental parameters including the initial H₂O₂ concentration, pH, catalyst dosage, initial dye concentration and the effect of ultrasonic power on the sonocatalysis of AO7 were examined. Different scavengers were used for removal of AO7 and their effects were also studied. Moreover, the removal of a number of organic dyes through sonocatalysis using ultrasonic irradiation technique in combination with synthesized CoFe₂O₄-rGO in aqueous solution was investigated. Furthermore, the possible sonocatalytic mechanism was also proposed for the removal of organic dyes. Finally, the removal by-products developed during the sono-Fenton-like system were also characterized by GC-MS technique.

2. Experimental

2.1. Materials

Cobalt(II) acetylacetonate (Co(acac)₃, 97%), iron(III) acetylacetonate (Fe(acac)₃, 97%), oleic acid (OAc, 90%), oleylamine (OAm, > 70%), benzyl ether (BE, 99%), 1,2-tetradecanediol (1,2-TDD, 97%), potassium permanganate (KMnO₄, > 99%), sodium nitrate (NaNO₃, > 99%), dimethylformamide (DMF, > 99%), hexanes (97%), isopropanol (99%), ethanol (99%) and acetone (97%) were purchased from Sigma-Aldrich and used as received. Natural graphite flakes were purchased from Alfa-Aesar®. Hydrogen peroxide (H₂O₂, 30%) and sulfuric acid (H₂SO₄, 95–98%) were purchased from Merck® and used without any purification. The organic dyes were purchased from Alvan Sabet Co. (Iran). Table 1 shows the structure and characteristics of organic dyes used as model pollutants.

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