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Modification of magnetite ore as heterogeneous nanocatalyst for degradation of three textile dyes: Simultaneous determination using MCR-ALS, process optimization and intermediate identification

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ABSTRACT

Degradation of mixture of three textile dyes (C.I. Basic Blue 3 (BB3), C.I. Basic Red 46 (BR46) and Malachite Green (MG)) was investigated simultaneously through the heterogeneous Fenton process. The investigated catalyst was natural magnetite nanostructures (NMNs) prepared by modification of natural magnetite microparticles (NMMs) by a green glow discharge plasma (GDP) technology. A complete characterization such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) analyses were executed to investigate various characteristics of the untreated and GDP treated-magnetite particles. The multivariate curve resolution with alternating least squares (MCR-ALS) modeling which is an important chemometrics technique was introduced and utilized as a novel method for multivariate calibration of the spectrophotometric data. The presence of four absorbing species were confirmed by MCR-ALS. In addition, by the use of this technique, the spectra and the concentration profiles of each dye were attained during the degradation process. A response surface methodology (RSM) was utilized to study, model and optimize the influence of several parameters on the dyes decolorization efficiencies. Also, the degradation by-products of the dyes generated during Fenton process were determined using gas chromatography coupled to mass spectrometry (GC–MS).

1. Introduction

Dyes, are the most widely used class of coloring materials because of their massive applications in various fields of science and technology. Most of the dyes are toxic and give an undesirable color to the receiving water bodies [1]. So, presence of the dyes or their degradation byproducts in industrial effluents causes a threat to human and environmental health. Thus, it is necessary to remove dyeing pollutants from wastewater before discharging them into the environmental water sources. The use of advanced oxidation processes (AOP's) has brought a novel evolution for the removal of resistance environmental pollutants [2–5]. AOP's degrade organic materials and convert them into CO_2 and H_2O by generating reactive oxygen species (ROS) with high oxidizing power. Recent studies indicate that the Fenton process, a subclass of AOPs, is a very convenient and efficient method for complete oxidation of various organic pollutants [6,7].

The reaction of hydrogen peroxide with ferrous or ferric ions has been known as homogeneous Fenton process. Homogenous Fenton process has some well-known advantages including the high efficiency of the process, utilizing of low cost reagents, its simple technology and the low toxicity of the initial reagents [8,9]. Whereas, the industrial application of the process is limited due to the necessity for a neutralization step, the use of large amount of iron salts, catalyst deactivation by some reagents such as phosphate ions and the narrow pH range (2.5–4) [10].

These problems have prompted researchers to begin studying on heterogeneous Fenton process. Heterogeneous Fenton process involves the use of natural and synthetic solid catalysts based on iron, including natural and synthetic zeolites modified with transition metals, iron-rich clay soils and natural mineral oxides such as magnetite, hematite and goethite [8,11,12].

Voelker and Kwan [13] have proposed the mechanism given in Eqs. (1)–(3) for generation of hydroxyl radicals ($^{\bullet}OH$) from hydrogen peroxide on the surface of solid iron-based catalysts:

$$Fe(II)_{surff} + H_2O_2 \rightarrow Fe(III)_{surff} + {}^{\bullet}OH + OH^- \quad (1)$$

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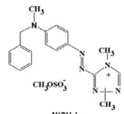
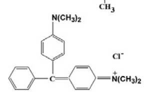
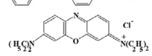
Table 1
Characteristics of the three textile dyes.

Dye	Chemical structure	Molecular formula	Color index number	λ_{max} (nm)	M_w (g/mol)
BR46		$C_{18}H_{24}N_6O_4S$	110825	530	420
MG		$C_{23}H_{25}ClN_2$	42000	619	364.91
BB3		$C_{20}H_{26}N_3OCl$	51004	654	360

$$Fe(III)_{surf} + H_2O_2 \rightarrow Fe(III)_{surff} - H_2O_2 \quad (2)$$

$$Fe(III)_{surf} - H_2O_2 \rightarrow Fe(II)_{surf} + HO_2^{\bullet} + H^+ \quad (3)$$

According to the related literature, the advantages of using solid iron-based catalysts in the Fenton process are the possibility of operating the process in wide range of pH and the reusability of the catalyst [14–16]. Also, utilization of the natural iron-based heterogeneous catalysts in Fenton process could be a potential alternative owning to their low cost and abundance [14,17]. Magnetite is not a toxic compound and causes no secondary pollution in the environment. Regarding these properties, natural magnetite was utilized as a heterogeneous catalyst in this work [18–20]. In spite of the mentioned properties for magnetite, yet some issues have remained. As an example, the specific surface area of natural magnetite is low. The low surface area of a natural heterogeneous catalyst can considerably reduce the catalytic activity in many catalytic reactions. However, nanomaterials could be a good choice for various catalytic applications due to the high specific surface area [21].

Recently, a wide variety of methods have been developed to produce magnetite nanostructures [22,23]. Despite the various advantages reported for the mentioned methods, they require costly and in some cases toxic precursors [23–25].

Newly, non-thermal plasma techniques consisting glow discharge, silent discharge and radio frequency (RF) discharge has been introduced as a green methods for synthesizing nanostructures [26–28], modifying the surface of the catalysts to increase the activity and the stability of the catalysts [29,30]. So, in the present study glow discharge plasma technique is utilized as a novel green method to produce natural magnetite nanostructures (NMNs).

Textile industries wastewater includes mixture of various kinds of dyeing pollutants. Therefore, it is essential to simultaneously remove the mixture of pollutants from the mentioned effluents. But, the limitation is this regard is that generally the spectrophotometric methods are used for determining the concentration of the remained dye in the system. However since the absorbance spectrum of several dyes overlap with each other [31], using the univariate calibration methods will not be possible [31]. Recently, first-order and second-order multivariate calibration methods including partial least squares (PLS) regression and multivariate curve resolution with alternating least squares (MCR-ALS) are developed for simultaneous analysis of compounds which spectra overlap with each other [32–34]. However, using PLS for multi-components analysis has some disadvantages such as it requires a large number of standard solutions as calibration set. Also, the chemical matrix of the calibration samples and the unknown samples should be the same.

Regarding the mentioned disadvantages, it can be concluded that utilization of PLS in the degradation systems cannot be efficient. This is because during oxidation of organic pollutants different un-calibrated components such as degradation by-products are produced.

In such processes, MCR-ALS, which is a second-order multivariate calibration method, could be a good alternative. This technique is able to extract the concentration and spectral profiles of the main species and the degradation by products from the data matrix without the necessity of knowing much information about the studied system by the user [35,36].

The work is devoted to study the efficiency of the Fenton process in the presence of natural magnetite nanostructures for simultaneous degradation of mixture of three dyes (BB3, BR46 and MG). Glow discharge plasma (GDP) was used for production of the NMNs. Also, a thorough characterization was operated to identify the physical and chemical properties of natural magnetite microparticles (NMMs) and NMNs. As a novel technique MCR-ALS was utilized for resolution and quantification of the dye in the mixtures, from the set of spectra achieved in the UV–vis spectrophotometer during the Fenton process. Then, central composite design (CCD) was designed to examine the effect of different operating factors and find the optimum conditions in which the removal efficiency of the three dyes is maximum. The degradation intermediates produced in the process were identified by gas chromatography coupled to mass spectrometry (GC–MS).

2. Experimental

2.1. Materials

H_2O_2 (30%), CH_3CH_2OH, NaOH and H_2SO_4 were obtained from Merck Co. (Germany). Natural magnetite ores was purchased from Sarab (Bijar) mine in the northwest of Iran. Other used reagents were of analytical grade and were used without further purification. The dyes (BB3, BR46 and MG) were purchased from Shimi Boyakhsaz Co. (Iran). Their properties are presented in Table 1.

2.2. Production of NMNs by GDP

NMNs were produced by modification of natural magnetite micro particles with N_2 gas GDP. Fig. 1 illustrates the GDP system used for preparation of NMNs. The GDP reactor was prepared from a Pyrex tube reactor with size of 40 cm × 5 cm and 2 aluminum bungs for fastening the sides of reactor and electrodes placed on the bungs for connecting to the capacitor in parallel. The plasma is generated along with discharge operations by the two electrodes linked to a DC high-voltage (1200–1300 V) power supply (Tabriz, Iran). Approximately 1 g of natural magnetite particles which were washed with distilled water. The dried catalyst was placed on mica sheets and situated in the plasma reactor next to the anodic electrode. To produce plasma, N_2 gas was entered to the tube