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Preparation of nanostructured magnetite with plasma for degradation of a cationic textile dye by the heterogeneous Fenton process

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ABSTRACT

The surface and catalytic properties of natural magnetite were modified using plasma treatment, and were characterized using X-ray diffraction, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, N_2 adsorption–desorption, and scanning electron microscopy. The results show the production of nanostructured magnetite, from its natural particles, with an average diameter in the range of 20–40 nm. The application of nanostructured magnetite in a heterogeneous Fenton process was investigated in the degradation of Basic Blue 3 (BB3) as a model pollutant in aqueous solution. The effects of operational parameters were studied with respect to decolorization efficiency. The application of a nanostructured magnetite catalyst allows the Fenton process to be operated at milder pH conditions (a pH of 5). A decolorization efficiency of 96% in the presence of plasma-treated magnetite was approximately two times higher than that of untreated magnetite. Negligible iron leaching and a simple separation of used catalyst using an external magnetite field are merits of using plasma-treated magnetite in heterogeneous Fenton process.

1. Introduction

Extensive consumption of synthetic dyes in various industrial processes such as those used in the textile, pharmaceutical, paper, food, and leather industries leads to the production of a considerable amount of wastewater polluted with these chemicals [1,2]. Usually, these dyes have stable chemical structures to suit various coloring applications [3]. Therefore, the discharge of wastewater containing these chemicals into natural streams reduces light penetration, and accordingly affects photosynthetic phenomena, and increases toxicity and chemical oxygen demand [4].

The treatment of industry wastewater containing dyes prior to discharge is essential. Various techniques such as electrodialysis [5], ion exchange [6], and adsorption [7] have been used for removing pollutants from aqueous environments. In recent years, advanced oxidation processes (AOPs) have been extensively studied and used for the removal of pollutants from water and wastewater. These methods, when performed under reasonably mild conditions of temperature and pressure, show high efficiency for the degradation of chemical pollutants [8]. In AOP processes, various materials and methods involve the formation of $^{\bullet}OH$ radicals in driving oxidation processes [9]. Among these AOPs, the Fenton reaction is considered to be an important source of $^{\bullet}OH$ radicals that are derived from the catalytic breakdown of hydrogen peroxide molecules in the presence of iron ions as a catalyst [10]. This process can be conducted in either homogeneous or heterogeneous forms. Homogeneous Fenton is a basic form of the process in which a soluble form of iron ions, especially Fe^{2+}, catalyze the formation of $^{\bullet}OH$. Many researchers have examined the homogeneous Fenton process as applied to chemical pollutants. The homogeneous Fenton process must be performed in a low and limited pH range of around 2.8 [11]. In addition, iron ions leave the solution in the form of iron-containing sludge [11]. Accordingly, further application of the homogeneous Fenton is limited. Novel approaches of applying the heterogeneous Fenton process to overcome these drawbacks are currently being examined. In this process, iron oxide particles or Fe ions immobilized on the surface and in the pore spaces of different solids catalyze the formation of $^{\bullet}OH$. Extensive research attention has been paid to investigate the ability of various heterogeneous Fenton processes in the removal of chemical pollutants from aqueous media such as the oxidation of paracetamol [12],

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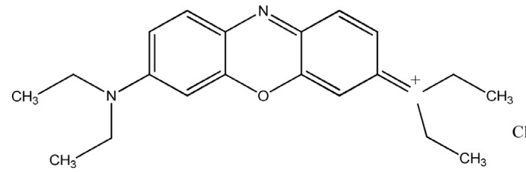
1876-1070/

Table 1
Structure and characterization of BB3.

Color index name	C.I. Basic Blue 3 (BB3)
Chemical structure	
Chemical class	Cationic, monoxazine
Molecular formula	$C_{20}H_{26}N_3OCl$
Color index number	51004
λ_{max} (nm)	654
M_w (g/mol)	359.89

the oxidation of monochlorobenzene [13], and the decolorization of a textile dye solution [2].

Fe^{2+} is more active in the Fenton reaction than other forms of iron. Thus, magnetite, which is the only pure oxide containing Fe(II) and Fe(III), is more appropriate to use in the heterogeneous Fenton process [14,15]. Other advantages of using magnetite in the Fenton reaction, such as the possibility of operating the process at a near-neutral pH and easy magnetic separation of used magnetite from treated solutions, make this iron oxide appropriate for use in successive treatment processes [14]. According to recent studies, it has been recognized that magnetite is an ideal catalytic material as compared with other heterogeneous catalysts [16].

A basic shortcoming associated with the heterogeneous Fenton process is high mass transfer resistance and low reaction rate compared to the homogeneous Fenton process. One effective method to address this shortcoming is the application of a nano-sized catalyst.

Magnetic nanoparticles can be prepared through different synthetic methods such as the chemical co-precipitation [17], sol–gel [18], and hydrothermal methods [19]. Increased efforts are under way to widespread more effective techniques in the preparation of magnetic nanoparticles. One potential technique is the use of plasma [2]. Plasma, which is known as the fourth state of matter, consists of positive and negative ions, electrons, radicals, atoms, and molecules in the form of ionized gases. The basic classifications of plasma treatments are high temperature and low temperature plasmas, which are used in nuclear applications and the processing of matter, respectively. Low temperature plasma is used in fast and clean treatment processes that are classified as thermal and non-thermal [20]. The use of non-thermal plasma for industrial applications is easier than the other approaches since it can be provided at low temperatures and pressures [21].

In this study, the nanostructured magnetite was used as the iron source in heterogeneous Fenton to degrade Basic Blue 3 (BB3) dye in aqueous solutions. This cationic dye is used in the textile industry for acrylic and wool fiber dyeing [22]. In Iran, BB3 has been extensively used in the carpet and blanket industries. Accordingly, in the present work, BB3 dye was selected as a model pollutant. The effects of the initial solution pH, dye concentration, H_2O_2 concentration, and magnetite dosage were investigated comprehensively in a series of decolorization efficiency batch experiments.

2. Materials and methods

2.1. Materials and reagents

Natural magnetite was taken from Sarab, Iran. C.I. BB3 was purchased from Boyakhsaz Co., Tehran, Iran. The chemical structure and characteristics of BB3 are shown in Table 1. Ammonia (25%), sulfuric acid (98%), hydrochloric acid (37%), sodium hydroxide (99%), hydrogen peroxide (30%), ammonium acetate, hydroxylamine hydrochloride, 1,10-phenanthroline, and sodium nitrate (99%) were obtained from Merck (Germany) and used without further purification. Ethanol was obtained from Jahan Alcohol Teb Co. (Arak, Iran). Distilled water was used throughout the investigation.

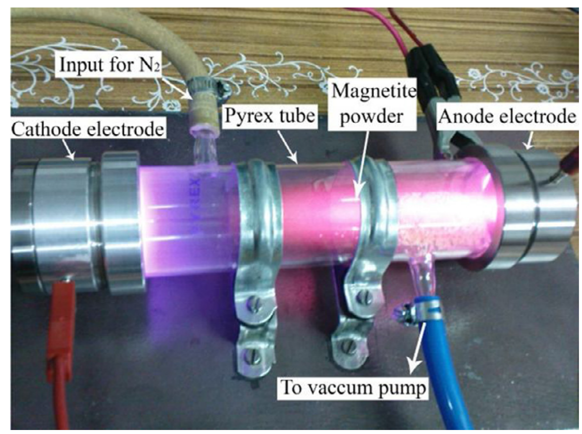


Fig. 1. The plasma system used in this study.

2.2. Plasma treatment procedure

In order to prepare nanostructured magnetite, glow discharge plasma in a nitrogen atmosphere was used. First, the mineral magnetite was taken from Sarab, Iran and crushed to prepare particles with diameters between 354 and 707 μm. The obtained particles were washed with distilled water and dried at 60–70 °C for 24 h. Three gram of magnetite particles were placed in a chamber in a plasma reactor that was made from a horizontal Pyrex tube with two electrodes on both sides (Fig. 1). The reactor was sealed, and nitrogen gas was pumped inside the reactor. The reactor reached low pressure using rotary and turbo-molecular pumps. Direct current (DC) was applied to the electrodes to generate plasma. After this process, the plasma-treated magnetite particles were collected for later use. By using glow discharge plasma, low cost gases (nitrogen gas in this case), and mineral magnetite, the production of nano-structured magnetite was realized for less than 0.047 US$/g.

2.3. Catalyst characterization

In order to identify the effects of plasma treatment on the characteristics of natural magnetite particles, the morphology and dimensions of the natural and plasma-treated magnetite samples were examined using scanning electron microscopy (SEM) (S-4200, Hitachi,