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Production of nanocatalyst from natural magnetite by glow discharge plasma for enhanced catalytic ozonation of an oxazine dye in aqueous solution

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ABSTRACT

Cheap natural magnetite (NM) was modified with oxygen plasma owing to its cleaning effect by chemical etching and with argon plasma due to its sputtering effect resulting in more surface roughness. These plasmas were utilized individually or in the order of first O_2 and then Ar plasmas, respectively. The performance of the plasma treated magnetites (PTMs) was higher than NM for treatment of Basic Blue 3 (BB3) in catalytic ozonation (O_3/PTM). The properties of NM and the most efficient treated magnetite (PTM_4) samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Brunauer–Emmett–Teller (BET) and scanning electron microscopy (SEM) methods. The optimal values were chosen for operational parameters including ozone concentration (0.3 g/L), initial pH (6.7) and PTM_4 dosage (600 mg/L). GC–Mass analysis was applied to detect intermediates. Environmentally-friendly treatment of the NM, simple separation of the catalyst, negligible leached iron concentration, successive reusability at milder pH and unaffected efficiency in the presence of inorganic salts are the main advantages of the PTM_4.

1. Introduction

Wastewater of textile industries have extensive amounts of various dyes, which are commonly bio-resistant and as a consequence conventional biological methods are not efficient for their remediation [1]. Moreover, other physico-chemical processes like adsorption and coagulation merely transfer pollutants to secondary phases, that need more treatment [2]. Hence, applications of advanced oxidation processes (AOPs) are more proper not only for degradation, but also for mineralization of diverse contaminants with no extra waste [3]. Among reactive oxygen species (ROS), hydroxyl radicals (•OH) have the significant role in AOPs due to unselective reaction with organic pollutants and their conversion to harmless compounds like carbon dioxide, water and inorganic mineral salts [4].

Ozonation treatment is one of the effective AOPs applied for the removal of persistent organic pollutants (POPs) due to its high reactivity and disinfection ability [4,5]. Degradation of POPs can be explained by decomposition of O_3 to generate •OH radicals in basic mediums (Eqs. (1) and (2)) or by its direct electrophilic attack in acidic conditions [6]. However, it has been known that the appropriate degradation of pollutants may be not achieved by O_3 alone process [7].

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (1)$$

$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^{\bullet -} + O_2 \quad (2)$$

Heterogeneous catalyzed ozonation, which can be performed under ambient conditions is more efficient process for the removal of organic pollutants like humic and oxalic acids [8]. It can be attributed to more ozone dissolution and decomposition in the presence of solid particles due to ozone reaction with hydroxyl groups, which is existed on the surface of particles [9].

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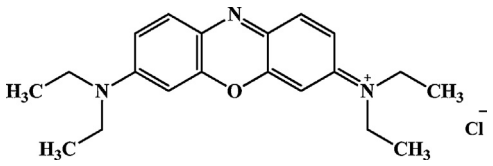

Fig. 1. Chemical structure of Basic Blue 3.

Stable form and abundance of magnetite (Fe_3O_4) makes it adequate for usage in the catalytic ozonation [10]. Furthermore, applications of nano-sized catalysts in heterogeneous ozonation results in more reaction sites and better mass transfer [8,11]. However, different synthesis methods for producing nano-sized magnetite require toxic and expensive reactants [10].

Plasma is ionized gas that it comprises from positive and negative ions, electrons and neutral species, which is considered as the forth state of matter, solves the above-mentioned problems by an environmentally-friendly method [12]. Recently, non-thermal plasma methods including glow discharge, silent discharge, and radio frequency discharge have been applied for surface modification of various catalysts and improvement of their performance [13,14]. For instance, the plasma treatment changes the surface structure and activity of synthesized zeolites or natural clinoptilolite [13]. Besides, stability and catalytic activity of the Pd/HZSM-5 catalyst enhance after treatment by plasma [15]. In addition, plasma-modified Fe_2O_3/ZSM-5 catalyst with the high activity and selectivity for hydrogenation of carbon monoxide is obtained using the glow discharge of oxygen and argon [16].

To the best of our knowledge, there have been no reports regarding to the surface modification of natural magnetite particles under the glow discharge plasma for using in water treatment process. So, in this study, first, a novel method to generate nanostructured magnetite utilizing the plasma method is presented. The characterizations of treated NM were performed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Brunauer–Emmett–Teller (BET) and scanning electron microscopy (SEM) methods. Then, the efficiency of PTM in heterogeneous catalytic ozonation for the decolorization of BB3 was evaluated and compared with NM. Finally, the effect of operational parameters include dye concentration, ozone concentration, initial pH, organic, PTM dosage and additional of inorganic salts were carried out and some of the generated intermediates during the process were identified by GC–Mass.

2. Experimental

2.1. Materials

Natural magnetite was provided from Sarab, Iran, which was very cheap and abundant. Elemental composition of NM was identified (O, 52.85%; Fe, 10.54%; C, 21.18%; Si, 14.25% and Ti, 1.18%) by X-ray photoelectron spectroscopy (XPS) using K-ALPHA Thermo Scientific spectrometer (UK). C.I. BB3 (color index number: 45170, molecular formula = $C_{20}H_{26}N_3OCl$, λ_{max} = 654 nm and M_w = 359.89 g/mol), which is a cationic mono-oxazine dye, purchased from Boyakhsaz Co., Iran. Its chemical structure is shown in Fig. 1.

BB3 is used extensively for dyeing of wool and acrylic fibers with lethal dose 50 (LD_{50}) of 100 mg/kg for rats [17]. All of the other chemicals were of analytical grade and they were provided from Merck, Germany.

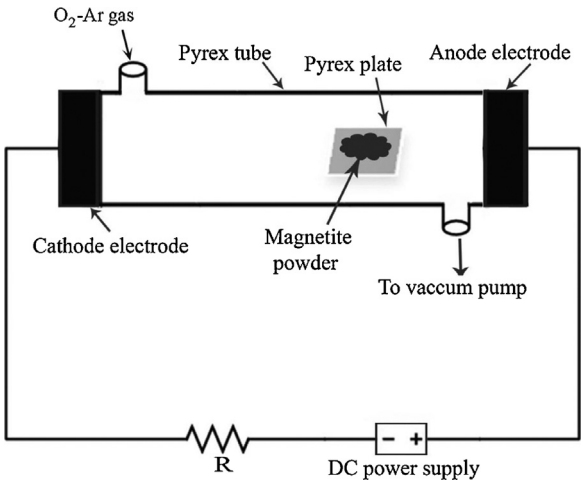

Fig. 2. Schematic diagram of the glow discharge plasma system.

Table 1
Effect of the different catalytic ozonation and ozonation on the apparent pseudo-first-order constants of degradation and mineralization of BB3.

No.	Process	Type and time of applied gases in plasma	k_{app} (min^{-1})	R^2
1	O_3	–	0.0510	0.96
2	O_3/NM	–	0.0734	0.98
3	O_3/PTM_1	O_2 (60 min)	0.1295	0.99
4	O_3/PTM_2	Ar (60 min)	0.1685	0.98
5	O_3/PTM_3	O_2 (45 min) + Ar (15 min)	0.1384	0.97
6	O_3/PTM_4	O_2 (15 min) + Ar (45 min)	0.1814	0.97

2.2. Procedure of catalyst treatment and characterization methods

NM sample was crushed to prepare particles with diameter between 210 and 354 μm and the obtained particles were washed with distilled water and they dried at 60–70 °C for 24 h. Then, non-thermal plasma technique was used for rejuvenation of them (3 g) using a plasma reactor made up of a Pyrex tube equipped with two electrodes on its sides (Fig. 2).

DC high-voltage (1200 V) was applied on electrodes to generate glow discharge plasma. Oxygen and/or argon at a flow of 3 standard cubic centimeters per second were fed to the plasma reactor individually to generate the plasma. Table 1 presents the type and applied time of the mentioned gases in the plasma reactor.

After the modifying process, the PTM particles were collected for using in heterogeneous ozonation. In order to characterization of NM and the most effective plasma treated magnetite (PTM_4), the following analyses were performed: (1) the phase identification was carried out by X-ray diffraction (XRD) technique (PANalytical X'Pert PRO, Germany) with Cu-kα radiation (45 kV, 40 mA, 0.15406 nm). (2) Fourier transform infrared (FT-IR) spectra of the samples were obtained by Tensor 27, Bruker spectrometer (Germany). (3) Scanning electron microscopy (S-4200Hitachi, Japan) was applied to identify their morphology and dimensions. (4) The porosity of the samples was evaluated by physical adsorption of N_2 at 77 K using Nitrometrics Gmini series (Japan). (5) the pH of point of zero charge (pH_{PZC}) was determined according to the salt addition method [18].

2.3. Catalytic ozonation set-up and procedure

The ozonation set-up is illustrated in Fig. 3.

Experiments were carried out in batch mode by a cylindrical reactor (Pyrex, 36 cm height × 4.5 cm internal diameter). To generate ozone, oxygen gas, which was provided by oxygen generator