Ultrasonics Sonochemistry 32 (2016) 357–370

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Heterogeneous sono-Fenton process using pyrite nanorods prepared by non-thermal plasma for degradation of an anthraquinone dye

Alireza Khataee [a,*], Peyman Gholami [a], Behrouz Vahid [b], Sang Woo Joo [c,**]

[a] Research Laboratory of Advanced Water and Wastewater Treatment Processes, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, 51666-16471 Tabriz, Iran
[b] Department of Chemical Engineering, Tabriz Branch, Islamic Azad University, 51579-44533 Tabriz, Iran
[c] School of Mechanical Engineering, Yeungnam University, 712-749 Gyeongsan, South Korea

ARTICLE INFO

Article history:
Received 20 January 2016
Received in revised form 1 April 2016
Accepted 3 April 2016
Available online 4 April 2016

Keywords:
Nanorods
Plasma-modified pyrite
Heterogeneous sono-Fenton
Non-thermal plasma
Degradation

ABSTRACT

Natural pyrite (NP) was treated using oxygen and nitrogen non-thermal plasmas to form modified catalysts. Cleaning effect of the O_2 plasma by chemical etching leads to removal of impurities from catalyst surface and sputtering effect of the N_2 plasma results in formation of pyrite nanorods. The mentioned plasmas were applied separately or in the order of first O_2 and then N_2, respectively. The catalytic performance of the plasma-modified pyrites (PMPs) is better than the NP for treatment of Reactive Blue 69 (RB69) in heterogeneous sono-Fenton process (US/H_2O_2/PMP). The NP and the most effective modified pyrite (PMP_4) samples were characterized by XRD, FT-IR, SEM, EDX, XPS and BET analyses. The desired amounts were chosen for operational parameters including initial pH (5), H_2O_2 concentration (1 mM), PMP_4 dosage (0.6 g/L), dye concentration (20 mg/L), and ultrasonic power (300 W). Moreover, the effects of peroxydisulfate and inorganic salts on the degradation efficiency were investigated. Gas chromatography–mass spectrometry (GC–MS) method was applied to identify the generated intermediates and a plausible pathway was proposed for RB69 degradation. Environmentally-friendly modification of the NP, low amount of leached iron and repeated reusability at milder pH are the significant privileges of the PMP_4. The phytotoxicity test using *Spirodela polyrrhiza* verified the remarkable toxicity removal of the RB69 solution after the treatment process.

1. Introduction

Textile industry wastewaters have large amounts of diverse dyes, which are generally bio-resistant and consequently conventional biological methods are not effective for their treatment [1]. Moreover, other physical and chemical processes such as coagulation and adsorption merely transfer pollutants to secondary phases, that require more remediation [2]. Hence, utilization of advanced oxidation processes (AOPs) are more appropriate not only to degrade, but also to mineralize various contaminants with no further waste [3]. Among AOPs, the Fenton and ultrasonic processes are easy and efficient treatment techniques that are widely used for the degradation of different contaminates in polluted water sources [4]. Hydroxyl radicals ($^{\cdot}OH$) as a reactive oxygen species (ROS) have the substantial role in AOPs owing to unselective attack to organic pollutants and their degradation intermediates to convert them to harmless compounds like carbon dioxide, water and inorganic mineral salts [5]. They can be produced by the heterogeneous Fenton reaction (Eq. (1)) or from water cleavage under ultrasonic waves (Eq. (2)) via cavitation phenomenon [6].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^{-} \tag{1}$$

$$H_2O \xrightarrow{)))} {}^{\cdot}OH + H^{\cdot} \tag{2}$$

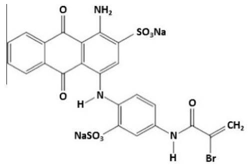
After directing ultrasonic irradiation into a liquid phase, the cavitation results in generation, growth, and eventually collapse of microbubbles forming high localized pressures and temperatures based on hot spot approach [7]. However, ultrasonic process consumes more energy and time in comparison of other methods in AOPs owing to its low degradation rate; thus it can be coupled with other processes such as Fenton process to enhance its performance for water treatment [8]. Moreover, it should be mentioned that catalyst recycling and also its separation from the treated water restrict the application of homogeneous Fenton process, which can be carried out in acidic medium (pH 3) to prevent from the precipitation of iron. Besides, usage of heterogeneous Fenton

---

* Corresponding author.
** Co-corresponding author.
E-mail addresses: a_khataee@tabrizu.ac.ir, ar_khataee@yahoo.com (A. Khataee), swjoo@yu.ac.kr (S.W. Joo).

http://dx.doi.org/10.1016/j.ultsonch.2016.04.002

Table 1
Characteristic of Reactive Blue 69.

Chemical structure	Molecular formula	Color index number	λ_{max} (nm)	M_w (g/mol)
	$C_{23}H_{14}BrN_3Na_2O_9S_2$	13429	604	666.39

process with no requirement for separation of catalyst, performing at milder pHs and low leached iron is another way to reduce these drawbacks [9].

Magnetite [10], goethite [11] and pyrite [12] are used as heterogeneous catalysts in Fenton process in which superficial Fe ions catalyze the generation of $^{\cdot}OH$. The pyrite (FeS_2) is the most plentiful and nontoxic metal sulfide in the earth [13]. The application of synthesized pyrite has been studied in water treatment processes including the Fenton and adsorption methods [14,15]. It should be noticed that the heterogeneous Fenton process has some confines compared to the homogeneous one like mass transfer resistance and limited active reaction sites. The effective solutions to overcome these obstacles are usage of nanostructured catalysts and sonication [16]. However, formation of nano-sized compounds by synthesis methods needs expensive and toxic reactants [17].

Plasma is an ionized gas composing of positive and negative ions, electrons and uncharged species, considered as forth state of matter. It is an environmentally-friendly way for formation of various nanostructures for different applications [18]; silent discharge, radio frequency and glow discharge techniques as non-thermal plasma method have been used for development of modified catalysts [19,20]. For instance, the surface area and activity of natural clinoptilolite and synthesized zeolites have been enhanced using plasma treatment [19]. The catalytic performance and stability of the Pd/HZSM-5 catalyst have been improved after plasma modification [21]. The hydrogenation selectivity of acetylene increases by using of the Ar, H_2 and O_2 atmosphere plasma for treated Pd/TiO_2 catalyst [22]. Modified magnetite by oxygen and argon glow discharge plasmas was utilized for degradation of an oxazine dye through catalytic ozonation [23]. Hydrogenation of carbon monoxide has been carried out using plasma-treated Fe_2O_3/ZSM-5 catalyst with high activity and selectivity prepared by the oxygen and argon glow discharge plasmas [24].

The purpose of this study is to modify the natural pyrite using the O_2 and N_2 glow discharge plasmas as the heterogeneous sono-Fenton catalyst. The characterization of NP and PMP_4 was performed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS) and Brunauer–Emmett–Teller (BET). Then, the efficiency of the modified catalyst for degradation of RB69 from aqueous solutions was evaluated and compared with the NP in US/H_2O_2/PMP process. The effect of operational parameters including the solution pH, H_2O_2 concentration, modified catalyst dosage, initial RB69 concentration, ultrasonic power, presence of peroxydisulfate enhancer, and inorganic salts were investigated on the degradation efficiency (DE%) of dye in a series of batch experiments. Gas chromatography–mass spectrometry (GC–MS) was used to verify the intermediates produced through the RB69 degradation and plausible degradation pathway was proposed. The phytotoxicity test was performed for the dye solution before and after treatment using *S. polyrrhiza* plant.

2. Experimental procedure

2.1. Materials

Natural pyrite was provided from Morvarid iron mine (Zanjan, Iran). The anthraquinone dye, Reactive Blue 69 was obtained from Ciba-Geigy ltd (Switzerland) used as a textile dye for silk and wool. The characterizations of RB69 are presented in Table 1. All of the chemicals were supplied from Merck (Germany). Distilled water was applied throughout the experiments.

2.2. Pyrite nanorods preparation

NP sample was crushed by rod and ball milling (Kian Madan Pars Co, Tehran, Iran) to form micro-grained pyrite particles with diameter between 149 and 297 μm. Then, the obtained particles were washed with distilled water and they dried at 70 °C for one day. Next, 3 g of the pyrite particles were placed in a plasma

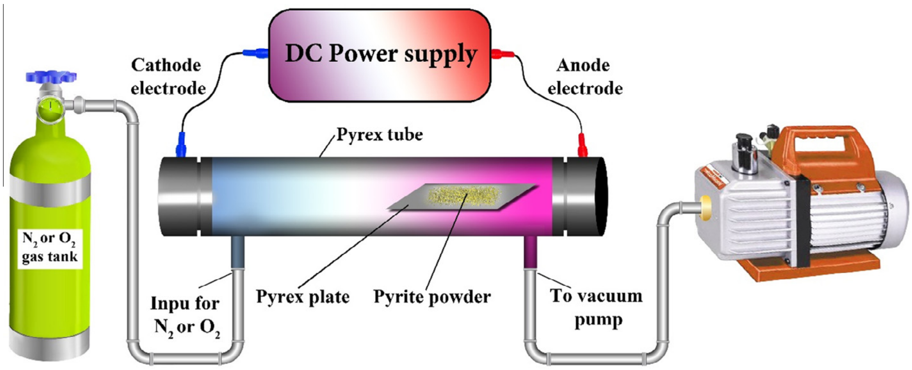


Fig. 1. Schematic diagram of the glow discharge plasma system used in this study.