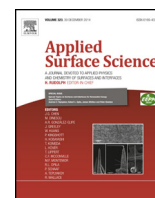




Contents lists available at ScienceDirect

Applied Surface Science

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



Catalytical degradation of relevant pollutants from waters using magnetic nanocatalysts

C. Nadejde^{a,*}, M. Neamtu^{a,*}, R.J. Schneider^b, V.-D. Hodoroaba^b, G. Ababei^c, U. Panne^{b,d}

^a Interdisciplinary Research Department – Field Science, 'Alexandru Ioan Cuza' University, Iasca Catargi 54, 700107 Iasi, Romania

^b BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, D-12205 Berlin, Germany

^c National Institute of Research and Development for Technical Physics, Dimitrie Mangeron Bd. 47, 700050 Iasi, Romania

^d Humboldt-Universität zu Berlin, Department of Chemistry, Brook-Taylor-Str. 2, 12489 Berlin, Germany

ARTICLE INFO

Article history:

Received 15 November 2014
Received in revised form 5 January 2015
Accepted 5 January 2015
Available online xxx

Keywords:

Sensitized magnetic nanocatalysts
Chemical synthesis
Structural characterization
Catalytic wet peroxide oxidation
Reactive azo dye degradation

ABSTRACT

The catalytic efficiency of two magnetically responsive nanocatalysts was evaluated for the degradation of Reactive Black 5 (RB5) and Reactive Yellow 84 (RY84) azo dyes using hydrogen peroxide as oxidant under very mild conditions (atmospheric pressure, room temperature). In order to obtain the nanocatalysts, the surface of magnetite (Fe₃O₄) nanoparticles, prepared by a co-precipitation method, was further modified with ferrous oxalate, a highly sensitive non-hazardous reducing agent. The sensitized nanomaterials were characterized by X-ray diffraction, scanning and transmission electron microscopy, energy-dispersive X-ray spectroscopy and vibrating sample magnetometry, and used in the catalytic wet hydrogen peroxide oxidation (CWHPO) of RB5 and RY84, in laboratory-scale experiments. The effect of important variables such as catalyst dosage, H₂O₂ concentration, and contact time was studied in the dye degradation kinetics. The results showed that it was possible to remove up to 99.7% dye in the presence of 20 mM H₂O₂ after 240 min of oxidation for a catalyst concentration of 10 g L⁻¹ at 25 °C and initial pH value of 9.0. CWHPO of reactive dyes using sensitized magnetic nanocatalysts can be a suitable pre-treatment method for complete decolorization of effluents from textile dyeing and finishing processes, once the optimum operating conditions are established.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Reactive azo dyes, currently considered the most problematic contaminants in the environment, are persistent and toxic synthetic compounds extensively used in industrial processes, over 20% of dye reaching the industrial effluents during fabrication procedures [1–4]. Once entered into environment, this type of dyes undergoes decomposition into potentially carcinogenic products [5–8]. Thus, they present major sources of water pollution, disturbing the ecosystem and leading to severe effects on living organisms [8–10].

Currently, a variety of water treatment methods was developed and are available for use [11–14]. However, many of these are inefficient or time consuming, since they do not destroy the pollutants in the reaction medium, but rather transfer them from one phase into another in a multi-step treatment procedure. The use of

heterogeneous catalysts has been proven as an attractive solution for decolorization and mineralization of dyes from waters [15–19]. Thus, catalytic wet hydrogen peroxide oxidation (CWHPO) of pollutants from waters has received great attention being efficient even in mild operating conditions.

A widely used type of heterogeneous catalysts are iron oxide based materials [20–22]. In the last years, magnetic nanostructures were often the materials of choice in environmental clean-up technologies due to their availability, low cost and environmentally friendly nature, their magnetic properties enabling them to be easily retrieved from the reaction medium [23]; furthermore, when their surface is modified with reactive non-toxic compounds, they become highly efficient catalysts able to remove recalcitrant organic pollutants from various media [24–26].

Although numerous studies regarding degradation of reactive azo dyes were reported in literature, there is a continuous search for safe materials with enhanced catalytical properties in order to optimize the decontamination through CWHPO, although most of the very efficient ones are produced or used in a non-economical manner. Nowadays, the eco-friendly materials have attracted a special interest, in the effort to minimize the negative impact

* Corresponding authors. Tel.: +40 232 202351; fax: +40 232 201202.
E-mail addresses: claudia.nadejde@uaic.ro (C. Nadejde),
mariana.neamtu@uaic.ro (M. Neamtu).

of technological processes in the environment. Among these, ferrous oxalate (FeC_2O_4) is a non-hazardous reducing agent able to react with oxidizing agents generating highly reactive oxygen species such as hydroxyl radical (HO^\bullet). Studies showed that iron oxide and oxalic acid can act together as a Fenton-like system (even without additional H_2O_2) to decompose organic pollutants in aqueous media [27,28]. The Fenton process uses hydrogen peroxide as oxidizing agent and a catalyst (most commonly a Fe^{2+} based material); in such systems, the oxidation of Fe^{2+} by H_2O_2 is an important source of HO^\bullet . Increasing the concentration of iron cations leads to a higher formation of hydroxyl radicals; this can be achieved by immobilizing ferrous oxalate onto magnetic iron oxide nanoparticles, so that oxalate will act as a scavenger of hydroxyl radicals produced in the Fenton reaction. The attacks by HO^\bullet radicals catalyze the oxidation of organic pollutants in the environment, resulting in an efficient pathway for non-biodegradable dye decomposition into non-harmful end products.

Since there is not sufficient reported data on the use of ferrous oxalate for the degradation of persistent pollutants in wastewaters, the present study aimed to find an alternative efficient solution to the current techniques for persistent pollutants removal in effluents, i.e. a non-hazardous, facile and inexpensive procedure to achieve fast complete degradation of reactive dyes from wastewaters, by using a sensitized nanocatalyst. Thus, two sensitized magnetic nanocatalysts having ferrous oxalate immobilized onto magnetite nanoparticles were prepared in different conditions by wet chemical synthesis in order to test and compare their performance in organic load reduction through CWHPO processes, as a function of their physico-chemical properties. Two commercial azo dyes, Reactive Black 5 (C.I.), RB5, and Reactive Yellow 84 (C.I.), RY84, were taken as substrate to simulate contaminated water samples. By monitoring the various factors controlling the degradation kinetics, the optimum experimental conditions for total dye degradation by $\text{Fe}_3\text{O}_4/\text{FeC}_2\text{O}_4$ nanocatalysts were established.

2. Materials and methods

2.1. Chemicals

Two azo dyes, Reactive Black 5 (color index, RB5) and Reactive Yellow 84 (color index, RY 84) were obtained from BASF (Germany) as commercially available dyes and used without further purification. All reagents of analytical grade were from Sigma-Aldrich and used as obtained in all experiments without additional purification. All solutions were prepared with distilled deionized water ($18.2\text{ M}\Omega/\text{cm}$), obtained with a Barnstead EASYpure[®] II Water Purification System.

2.2. Characterization

X-ray diffraction (XRD) analysis (Shimadzu LabX XRD-6000 diffractometer with $\text{Cu-K}\alpha$ radiation, $\lambda = 1.54\text{ \AA}$, scan range (2θ) from 20° to 70°) was employed in order to obtain information regarding the samples' crystallinity. The Scherrer formula was applied based on the data from the recorded XRD patterns in order to estimate the crystallite mean diameter in the synthesized samples.

A high-resolution Zeiss scanning electron microscope (SEM) of type Supra 40 (Carl Zeiss, Oberkochen, Germany) equipped with a Schottky field emitter was employed to characterize the sample surface morphology down to the nanometer scale. The SEM was equipped with an SDD EDS (energy dispersive X-ray spectrometer with silicon drift detector) spectrometer of type XFlash[®] 5010, from Bruker (Berlin, Germany). With this EDS system, a semi-quantitative analysis of the elemental composition of

the samples, being characterized by a rough surface morphology, was performed. High-resolution transmission electron microscopy (HRTEM) was conducted out on a ZEISS Libra 200 MC TEM/STEM electron microscope operating at 200 kV. The samples for TEM were deposited directly on carbon-copper grids. Vibrating Sample Magnetometer (VSM) System, MicroMag Model 2900/3900, was used for the measurement at room temperature of the magnetic properties of the obtained nanomaterials.

2.3. Experimental procedures

2.3.1. Synthesis of Fe_3O_4

The co-precipitation method was chosen for the fabrication of magnetite (Fe_3O_4) nanoparticles (NPs) due to its numerous advantages such as efficiency, rapidity, simplicity and low cost.

During the experimental procedure (performed at room temperature), three solutions of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (134 mM), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (67 mM) and NaOH (2 M) were prepared in distilled deionized water (DDW). The first two solutions of iron precursors in the stoichiometric ratio of 2:1 of Fe^{3+} and Fe^{2+} salts were mixed together under constant vigorous magnetic stirring and heating (to 75°C), followed by the dropwise addition of the alkaline precipitation agent (NaOH solution) into the homogeneous mixture. The constant stirring and temperature (75°C) were maintained for 30 min longer after the solution turned black (indicating the formation of iron oxide NPs, $\text{pH} \sim 12$) in order to ensure complete magnetite crystals formation. The resulted mixture was subjected to repeated alternating magnetic decantation and washing with DDW in order to remove impurities; the last washing step was carried out with absolute ethanol for the final product purification. The fine powder of magnetic iron oxide nanoparticles was obtained by drying the resulted black slurry in vacuum at 50°C .

2.3.2. Surface modification of Fe_3O_4 with ferrous oxalate

The magnetic catalysts (MC) of core/shell type structure were prepared in a post-synthesis procedure by immobilizing the reactive ferrous oxalate onto the as-synthesized magnetite nanocores, as described in the following: two samples were prepared using different proportions of the two types of materials composing the core/shell system. During the synthesis protocol, Fe_3O_4 dried powder and, respectively, ferrous oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) powder, were separately suspended in DDW with constant mechanical stirring and heating up to 75°C .

- The first sample (MC1) was obtained by gradually adding the ferrous oxalate into the black slurry while maintaining constant heat and thorough mechanical stirring, using a $\text{Fe}_3\text{O}_4:\text{FeC}_2\text{O}_4$ ratio of 8.5:1 (w/w).
- For the second sample (MC2), the Fe_3O_4 aqueous suspension was slowly poured into the FeC_2O_4 solution (at 75°C) with continuous mechanical stirring, in a 3.5:1 (w/w) ratio between magnetite and ferrous oxalate.

After two hours of continuous mechanical stirring and constant temperature, the two obtained products were rinsed several times with DDW and absolute ethanol (to remove impurities), followed by drying in a vacuum oven at 50°C . The finely ground powder was ready for further use in the catalytic experiments of dye degradation.

2.3.3. Catalytic experiments

The degradation by CPHWO processes of two commercially available reactive azo dyes (C.I. Reactive Black 5, RB5, and C.I. Reactive Yellow 84, RY84) was investigated in the framework of this study. The chemical structures of the two dyes are given in Fig. 1.

Download English Version:

<https://daneshyari.com/en/article/5357003>

Download Persian Version:

<https://daneshyari.com/article/5357003>

[Daneshyari.com](https://daneshyari.com)