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Facile synthesis of Fe_3O_4 nanoparticles via aqueous based electro chemical route for heterogeneous electro-Fenton removal of azo dyes

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ABSTRACT

Ferro magnetic iron oxide (Fe_3O_4) nanoparticles (NPs) were prepared through a facile and inexpensive electrochemical method. Characterization studies on the generated magnetite nanoparticles (MNPs) was carried out using X-Ray diffraction pattern (XRD), Fourier transform infrared (FTIR), field emission scanning electron microscope (FESEM), dynamic light scattering (DLS) and vibrating sample magnetometer (VSM) analysis. The synthesized material was used as a heterogeneous electro-Fenton catalyst in order to decolorize C.I. Acid Red 14 and C.I. Acid Blue 92 solutions. Graphite electrode Modified with carbon nanotubes (CNTs) were used as cathode in both synthesis and electro-Fenton processes. The effect of operational factors like pH range, initial dye concentration, Fe_3O_4 loading, current intensity and electrolyte (NaCl) dosage on dye removal efficiency was investigated. Remarkable discoloration in wide range of pH illustrated the superior catalytic potential of MNPs. Furthermore, the recyclability of Fe_3O_4 NPs after magnetic separation, the prevention of their entrance into the environment as a secondary pollutant and the promoted electro generation of hydrogen peroxide at the surface of cathode due to the presence of CNTs are the additional advantages of this study.

1. Introduction

It is impossible to ignore the role of clean water in human life and natural environmental. The presence of recalcitrant organic compounds in water causes environmental problems, which is due to by their toxicity, mutagenicity and carcinogenicity potentials. They also disrupt micro-organisms and aquatic life in general. Due to the pure water scarcity, it is still vital to develop novel and efficient wastewater treatment systems by finding new promising materials and methods [1–3].

Oxidation technologies are outstanding for the remediation of wastewater particularly the advanced oxidation processes (AOPs), in which oxidation takes place with higher efficiency compared to the conventional techniques [4]. One of the most desirable AOPs with impressive decontamination of wastewater containing toxic and persistent pollutants such as synthetic dyes is electro-Fenton. This eco-friendly method is a Fenton based process which is being demanded recently due to its considerable advantages. There is more control on the process and electricity is a clean source of energy, and by *in-situ* electro generation of H_2O_2 the reaction is not limited by storing and transferring the concentrated H_2O_2 solutions [5,6].

In spite of the fact that equations show the complex mechanism of Fenton consisting of chain reactions to produce destructive and efficient free radicals, Fenton is a simple and non-toxic reaction with no residue. Free radicals such as hydroxyl radical, can degrade the organic pollutants such as dyes and pigments present in the wastewater until their complete mineralization [7–9].

Various types of electrodes are employed to reduce oxygen to hydrogen peroxide in electro-Fenton process. Carbon and graphite electrodes are widely used in electrochemical processes, because they are abundant, inexpensive, chemically inert, and more over they have high surface area. The surface modified graphite electrode with carbon nanotubes (CNTs) are reported to be beneficial to promote the conductivity, stability, interacting surface area and the number of active sites for electro generation of H_2O_2. In general, CNTs structure can improve the electrochemical performance, and it is possible to increase the electron transfer between the reagent and electrode and accelerate the rate of the reactions [10–13].

Recently Magnetic iron oxides have attracted a great attention due to their remarkable properties such as being separable, strong recycling performance, large surface area, non-toxicity, biocompatibility, distinct colors, and stability in wide range of pH and temperature. Among various nano iron Oxides, ɣ-Fe_2O_3 (Meghamite)

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and Fe_3O_4 (Magnetite) have shown extraordinary magnetic and electrochemical properties. These magnetic iron oxides have attracted tremendous researchers interest. The commonly investigated fields for Fe_3O_4 are biomedical applications like Magnetic Resonance Imaging (MRI), drug delivery or magnetic drug targeting, cancer diagnosis and magnetically medicated separation of biomolecules, biosensors, high density magnetic data storage, magnetically controllable single electron transistor devices, magnetic inks and pigments to obtain black, Brown and red color, coating, catalysts and treatment of wastewater. Furthermore, the catalytic activity of the nano-sized magnetite along with facile preparation, eco-friendly characteristics, low cost and easy separation from solution by external magnetic field make them a promising candidate for wastewater treatment applications [14–18].

One the other hand, there is a big challenge to optimize the synthesis conditions to achieve iron nanoparticles due to their colloidal behavior, but the main demand is obtaining controlled synthesis in different features like dimension, morphology, chemical composition and capability of regeneration of nanoparticles or reproducibility of the reactions [17,19].

Magnetite nanoparticles (MNPs) can be produced by a variety of synthetic routes, including co-precipitation, thermal decomposition, hydrothermal reactions, sol-gel method, micro-emulsion technique, electrochemical procedure, etc. Nowadays there is a particular interest in electrochemical method due to their preferable features. Fabrication of magnetic iron oxide nanoparticles by this method is facile, fast, cost-effective, and electrochemical procedure can control the particle size by adjusting the applied current density, potential and also the distance between the electrodes [16,20,21].

There is a huge attention toward the heterogeneous Fenton reaction compared to the conventional homogeneous Fenton. Heterogeneous catalysts are more efficient in the degradation of organic pollutants like dyes in wastewater with more benefits such as its more possibility to be used in extended pH range which seems to be the main reason for applying heterogeneous catalysts. Several researches have reported an account of fundamental merits of different heterogeneous catalysts that are mainly:

(1) Preventing the formation of iron hydroxide sludge and associated issues (inhibition of UV radiation that influences the photo-Fenton process)
(2) No requirement for acidification and further neutralization
(3) Easy and inexpensive separation and recycling of the remained catalyst [15,22,23].

Among different heterogeneous catalysts, Fe_3O_4 nanoparticles have demonstrated high activity in oxidation processes based on their redox behavior. Abundance and high solubility rate compared to the other iron oxides and the presence and availability of Fe^{2+} in octahedral structure of these nanoparticles, which improve the Fenton reaction efficiency are the extraordinary properties of magnetic Fe_3O_4 nanoparticles [15,24]. The main reactions of heterogeneous electro-Fenton process are presented in Eqs. (1) and (2) and also Eq. (3) happens in surface of the cathode, can lead to

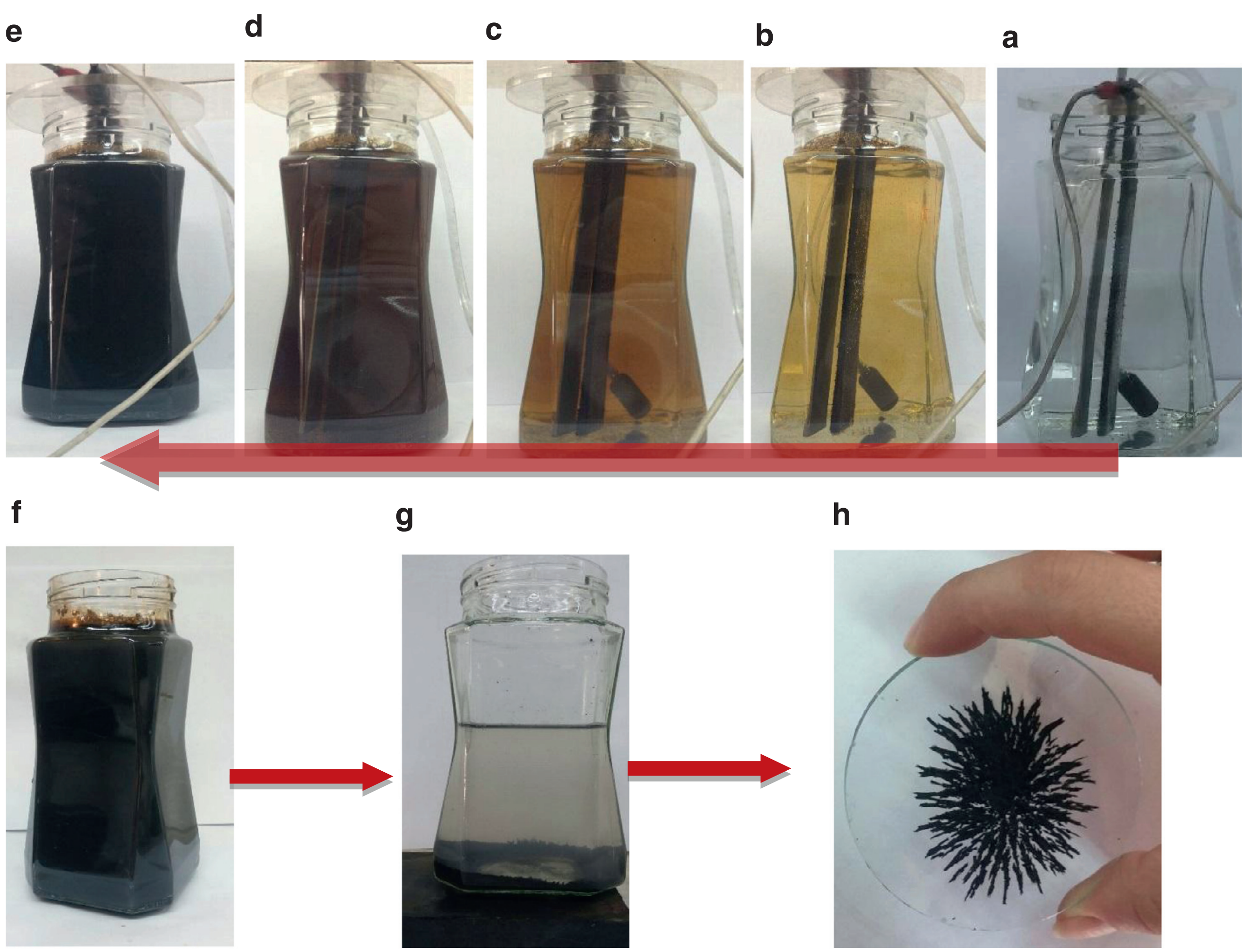

Fig. 1. The synthesis of Fe_3O_4 nanoparticles by electrochemical method, a) $T=T_0$, b) $T=1$–2 h, c) $T=2$–2.5 h, d) $T=2.5$–3.5, e) $T=3.5$–6 h, f) the end of synthesis process (removing imposed voltage), g) applying magnetic force and h) dried Fe_3O_4 Nano particles.

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