Alizarin Red S Dye Degradation by Using Bimetallic FE/NI Nanocatalyst at Room Temperature

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ABSTRACT

The present study was carried out to better understand the reactivity of nanoscale Ni/Fe particles towards the degradation of alizarin red s, a monoazo dye, in aqueous solutions was investigated using as synthesized and stored Fe-Ni bimetallic nanoparticles. UV-VIS analysis of the degradation products showed that as synthesized nanoparticles reductively cleaved the azo linkage to produce aniline as the major degradation product. However, 1-year-stored nanoparticles showed an oxidative degradation of alizarin red s through a hydroxyl-radical induced coupling of parent and/or product molecules. Reductive dye degradation using as synthesized nanoparticles proceeded through hydride transfer from nickel, whereas formation of a Fe²⁺-Ni⁰ galvanic cell in stored nanoparticles generated hydroxyl radicals from water in a non Fenton type reaction.

Keywords: Fe/Ni bimetallic nanoparticles, Alizarin red s dye, zerovalent iron (ZVI), Catalytic Dye degradation.

1. INTRODUCTION

Pollution of plane and ground water with the industry effluents is a major problem to public health. Synthetic dyes, suspended solids, dissolved chemicals are the main carcinogenic pollutants originate in textile and dying effluents. The degradation of some dyes take place to make toxic and hazards products. In addition the coloured pollutants decrease light diffusion & prevent photosynthesis. Alizarin red-S dye is one of them produce ‘red and’ purple coloured solution depending on pH of water. Many predictable methods for the removal of dying effluents from aqueous solutions can be divided into three classes; physical, biological
and chemical treatments.\textsuperscript{4,5} Physical adsorption is considered to be competitive & cost effective and efficient process for the removal of dyes. Moreover activated carbon is the most acceptable adsorbent and has been used for the adsorption of different chemicals from aqueous solutions.\textsuperscript{6,7} Alizarin red-S is used in large quantities in dying industries & produces several environment problems. To discover suitable & cost effective adsorbent is an important consideration for designing a suitable adsorption method to reduce water pollution. The objective of this study was to examine the possibility of use of nano crystalline Fe/Ni as a new adsorbent for the significant removal of alizarin red-S from aqueous solution. The equilibrium study is investigated to observe the effects of various process parameters such as pH, contact time, initial dye concentration temperature & the sorbent dosage on the adsorption process. Fe-Ni have been synthesized to improve the performance of the zerovalent iron (ZVI) technology for remediation of groundwater contaminants like chlorinated aliphatics,\textsuperscript{8-12} chlorinated aromatics\textsuperscript{13,14} and chlorinated pesticides.\textsuperscript{15,16} The advantages of bimetallic nanoparticles contain (a) higher surface area and density of reactive surface sites; (b) catalytic effects contributed by the lower hydrogen over-potential metal, which is effective in hydro dehalogenation reactions; and (c) inhibition of the corrosion products from accumulating on the surface reactive sites of ZVI. In all iron-based bimetallic systems, the catalytic metal (Pd, Pt, or Ni) enhances the formation of atomic hydrogen or hydride on the surface, and changes the electronic properties of iron, which is the electron donor and reductant for water. This facilitates the transfer of electrons and atomic hydrogen to the chlorinated compounds. Hence, the reductive degradation mechanism is the only pathway for obliteration of various halogenated organic compounds (HOCs).\textsuperscript{17-21} However, in addition to its reducing capability, iron nanoparticles (nZVI) also possess a capability to oxidize organic compounds in the presence of oxygen as a result of an induction of Fenton reagent chemistry.\textsuperscript{22,23} In this paper, Fe-Ni nanoparticles (<100 nm diameter) were preferred to study their reductive and/or oxidative degradation capacities.

2. EXPERIMENTAL PROCEDURE

Materials

Powder form of Synthesised pure Fe:Ni bimetallic nano composite, Alazarin red S (MW=320.271g/mol, C_{14}H_{7}NaO_{7}S, λ max =360nm)

Dye solution Preparation

A stock solution of 20 ppm alizarin red s dye was prepared. 100 ml of 20 ppm alizarin red s dye solution and 20 mg of Fe/Ni catalyst are taken in a 250 ml beaker. At room temperature the reaction mixture was continuously mechanically stirred to obtain uniform suspension. 5 ml of the above reaction mixture was taken and centrifuged and the absorbance is measured by using UV spectrophotometer. The stirring process is continued and the absorbance value was measured for 5 ml reaction mixture every 5 minutes until the colour degraded. A gradual decrease in the absorbance values were observed. The degradation of
Alizarin red S follows first order kinetics that obeys the equation $\ln(C_0/C) = kt$, where $k$ is the rate constant, $t$ is the irradiation time, $C_0$ and $C$ are the initial and concentration at time $t$. The first order rate constant value was high for the Fe:Ni (1:2) when compared to 2:1,1:1,1:0,0:1 Fe:Ni composition. Among of these catalysts 1:2 (Fe:Ni) has the highest rate constant has highest activity, highly efficient, nontoxic and chemically stable catalyst because of larger surface area of this catalyst causes greater adsorption of the dyes, further studies were carried out by using the same catalyst Fe:Ni(1:2). Comparative graph of Fe/Ni nano composite have been represented in Fig. 2.

![Comparative graph of Fe/Ni nano composite](image)

**Fig. 2 Comparative graph of Fe/Ni nano composite**

### 3. CHARACTERIZATION

**SEM (Scanning electron microscope)**

The morphology of the as-synthesized samples were investigated by field emission scanning electron microscopy (FE-SEM, LEO1550). For many nanotechnology developers looking at fundamental size and shape properties SEM may offer better performance for surface and shape analysis, particularly in applications such as quality control of colloidal nano-precipitates or for measuring surfaces and microstructures of nano sized powdered materials. The nano structures and morphologies of samples were examined by SEM characterization.

**UV-Visible spectral changes**

Ultraviolet/visible spectroscopy can also be used to study reaction rates. If a reagent or a product of the reaction absorbs radiation at a particular frequency the spectrometer can be set to measure the absorption at that frequency as a function of time. The absorption peaks corresponding to dye, diminished and finally disappeared under reaction which indicated that the dye had been degraded. The spectrum of alizarin red s in the visible region exhibits a main band with a maximum at 360 nm. The decrease of absorption peaks of alizarin red s at $\lambda_{\text{max}}$
= 360 nm in this figure indicated a rapid degradation of alizarin red s dye. Complete degradation of alizarin red s was observed in 90 min in the optimized conditions.

4. RESULTS AND DISCUSSIONS

4.1 SEM (Scanning electron microscopy)

Morphology study

The nano structures and morphologies of samples were examined by SEM characterization, carried out on S-3700. Morphology study Figure 4.1 (a to e) shows the SEM picture of the different ratios of nano Fe:Ni samples. From the images it can be clearly observed that the prepared samples consists of nano particles in the size of <100 nm. SEM studies were carried out to find out the surface morphology of synthesized Fe & Ni nanocomposite. SEM micrographs of the Fe & Ni nanocomposite have been represented in Fig. 4.1

![SEM images of Fe/Ni nanocomposites a) 0:1 ratio b) 1:0 ratio c) 1:1 ratio d) 1:2 ratio e) 2:1 ratio](image)

Fig. 4.1 SEM images of Fe/Ni nanocomposites a) 0:1 ratio b) 1:0 ratio c) 1:1 ratio d) 1:2 ratio e) 2:1 ratio

4.2 UV –Visible spectral changes a) Effect of initial concentration of alizarin red s on catalytic degradation

The degradation efficiency of alizarin red s was found to decrease with an increase in the initial dye concentration. The influence of dye initial concentration on catalytic degradation of alizarin red s was studied in the concentration range of 10 ppm to 40 ppm. Concentration had a significant effect on the degradation of alizarin red s. After illumination
for 90 min, the rate constant ‘k’ for 10, 20, 30, 40 ppm clearly shows that as the concentration decreases rate constant increases. This can be attributed to the hindering of photons with the increase in concentration of alizarin red s to reach the surface of catalyst. Moreover, as the concentration of dye alizarin red s increases, the molecules adsorbed on the surface of catalyst might increase. This decreases the active sites on the catalyst which results in a decrease in generation of hydroxyl radical, and hence the lower activity. Comparative graph have been represented in Fig. 4.2.a

![Graph](image1.png)

**a) Effect of initial concentration of alizarin red s on catalytic degradation**

**b) Effect of catalyst amount on degradation rate**

The degradation efficiency of alizarin red s is found to increase with an increase in the catalyst loading. The total active surface area increases with increasing catalyst dosage. When the dye concentration is increased the catalyst amount is constant, it results fewer active sites for the reaction, with the increased dye molecule the solution become more intense colour. The increase in degradation rate with the catalyst amount can be explained in terms of availability of active sites on the catalyst surface. The tendency of adsorption of the dye to the surface of the catalyst increases degradation efficiency. Comparative graph have been represented in Fig. 4.2.b

**c) Effect of PH on degradation rate**

The effect of pH on the decolourization of dye experiments were carried out at various pH values, ranging from 2-9 for constant dye concentration (20 ppm) with catalyst loading (20 mg). Similar behaviour has also been reported for the catalytic efficiency of (Fe: Ni) for decolourization of azo dyes. The interpretation of pH factor on the efficiency of photo catalytic degradation process can be explained on the basis of acid base property of metal oxide surface and the ionization state of ionisable organic molecule. In acidic solutions degradation
efficiency was more than that in alkaline solutions. The experimental results showed that higher degradation of dye occurred in acidic region than in a basic solution. The rate of decolourization increased with decrease in pH, exhibiting maximum efficiency (98.5%) at pH 2. Although the adsorption of dye molecules are low at alkaline pH, the possible reason for this behaviour may be the formation of more *OH radicals. At alkaline mediums, excess of hydroxyl anions facilitate generation of *OH radicals which is accepted as primary oxidizing species responsible for catalytic degradation, resulting in enhancement of the efficiency of the process. Comparative graph have been represented in Fig. 4.2.c

5. CONCLUSIONS

The results presented in this paper indicated that Pure nano Fe/Ni could be efficiently used to degrade the alizarin red s dye. The degradation kinetics of alizarin red s dye was fast with maximum efficiencies of 92.78% in 90 min using Fe:Ni(1:2) catalyst. The degradation rate of dyes was obviously affected by the operating parameters (illumination time, initial dye concentration, and amount of catalyst, pH and the band gap of semiconductors). Study of effect of pH revealed that the acidic pH favours the degradation of alizarin red s due to better Fe/Ni surface. The aim of this research is to study the degradation efficiency of the commercially available catalysts in the market in term of percentage of dye removal from real textile wastewater of Fe/Ni. In addition, effect of particles size on catalytic activity was also reported and discussed.

6. REFERENCES
