THE USE OF Ni$_x$Zn$_x$Fe$_2$O$_4$ IN THE REMOVAL OF CONGO RED

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ABSTRACT

Congo red is an organic dye used as a representative for organic contaminant of water; the prepared magnetic Nano particles is used in the removal of Congo red under many parameters including pH and the Ni$_x$Zn$_x$Fe$_2$O$_4$ concentrations. The results show that Congo red (CR) removal was succeeded using photo degradation method in the presence of Ni$_x$Zn$_x$Fe$_2$O$_4$ as a catalyst. It succeeded to eliminate about 97% of 40 ppm CR after 3h. Photo catalytic degradation of CR could be carried out successfully over a pH range form 6-10. The pH affects not only surface properties of Ni$_x$Zn$_x$Fe$_2$O$_4$ nanoparticles but also the dissociation of dye molecule and the formation of the hydroxyl radical.

Keywords: Ni$_x$Zn$_x$Fe$_2$O$_4$, Congo red, Photo degradation, magnetic nanoparticles, Co-precipitation

1-INTRODUCTION

Water is the source of life on earth. It covers more than 75% of it and provides the suitable environment for the living organisms. Water forms
nearly 80% of the cell mass [Brar et al; 2010]. Fresh water deficiency is a
definition for water shortage or crisis as there is a shortage of access to fresh
and potable water [Mahmoud et al; 2013]. This expression also refers to the
pollution of the present water sources and to the difficulty in obtaining fresh
water [Jumeria et al; 2014].

The main source for water pollution is from fertilizers and pesticides
generated from industrial, farms and human wastes which dumped into rivers
and lakes without proper treatments, other sources are oil spill on the ground
and waste water leakage from landfills which may goes underground and
pollute the underground water sources [Aoa et al; 2008].

Highly colored waste existence is of great importance as it prevent
penetration of light thus affects the biological process within water stream.
Beside that some dyes are carcinogenic and toxic [Sua et al; 2012]. It is
estimated that 10-50% of the dye is lost in the effluent [Rahimi et al; 2011].

Ni$_x$Zn$_x$Fe$_2$O$_4$ is used in hardness natural organic compounds and
alkalinity removal, decolorisation of pulp mill effluent and desalination
[Chenga et al; 2015]. After adsorption, Ni$_x$Zn$_x$Fe$_2$O$_4$ can be removed from the
medium by a magnet. It is a nontoxic, scalable economic and efficient
method. Synthesis of Ni$_x$Zn$_x$Fe$_2$O$_4$ nanoparticles is highly preferred for
potential application and fundamental research [Li et al; 2011].

Properties of Nano-ferrites such as (structural, magnetic, electrical,
dielectric, optical etc.) are very sensitive to the preparation method and other
synthesis parameters. Therefore, the selection of an appropriate synthesis method is the key to obtain high quality ferrites. [Aoa et al; 2008].

2-EXPERIMENTAL WORK

Basic data about chemicals, equipment and instruments are given. Also, procedures for evaluation of the photocatalytic potentials of Zn$_x$Ni$_{(1-x)}$Fe$_2$O$_4$ nanoparticles for selected contaminants are demonstrated. Additionally, the different possible parameters affecting photocatalytic efficiency are reported.

2.1 Chemicals

All the chemicals used in the experimental work were used directly without any additional purification or treatment. Table (1) summarize all the chemicals utilized in this work during different steps, indicating their specified purities, grade, and suppliers.

2.2 Types of the used contaminants

2.2.1 congo red

Congo red is an organic compound, the sodium salt of 3,3’-([1,1’-biphenyl]-4,4’-diyl)bis(4-aminonaphthalene-1-sulfonic acid)(figure 1). It is an azo dye. Congo red is water-soluble, yielding a red colloidal solution; its solubility is greater in organic solvents [Di Paolaa A et al ; 2011 and Praveena1 et al; 2015].

2.3 Nano ferrite preparation

Iron (III) nitrate, Fe(NO$_3$)$_3$·9H$_2$O, nickel(II) nitrate, Ni(NO$_3$)$_2$·6H$_2$O, and zinc nitrate, Zn(NO$_3$)$_2$·6H$_2$O were purchased from Acros Organics and PVP
(MW = 10,000) was supplied by Sigma Aldrich. All the chemical re-agents were of research grade and used without further purification. 3 g of PVP was dissolved in 100 ml of de-ionized water at 343 K before mixing 0.2 mmol of iron (III) nitrate, 0.025 mmol of nickel nitrate and 0.075 mmol zinc nitrate and the solution stirred for 2 hours. No precipitation occurred in the solution. The brown solution was poured into a glass Petri dish and heated at 353 K in an oven for 24 hours to release most of the water. The brown solid material was crushed into powder and the samples were heated for 3 hours in alumina boat at different calcination temperatures of 723, 773, 823 and 873 K to decompose the organic matters and crystallize the nanoparticles. [Pete nele et al; 2014]

2.4 Photo catalytic reactor

The removal of the contaminants by ultraviolet illumination which is called the photo catalytic process. Also, the photolysis of the contaminants was reported. In order to achieve a full evaluation of the synthetized Nanoferrite. The used UV reactor was a simple home made one. It consists of a glass measuring cylinder (100ml) having dimensions of 27 cm length, and 3 cm diameter. Figure (2) represents a full detailed description of the Photo catalytic Reactor setup.

To perform the photo catalytic decomposition experiments, the contaminants solutions and a certain amount of catalyst were loaded into the reactor.

Prior to the UV irradiation, aliquots of 1 ml suspension were sampled using a syringe at specific time intervals for analysis.
The photo decomposition efficiency (Removal %) was calculated from the following equation:

\[ \text{Removal \%} = \left(1 - \frac{C_t}{C_o}\right) \times 100 \]

Where \( C_o \) is the initial concentration of the contaminant (mg/l), and \( C_t \) is the concentration at time (t).

In the process of photo catalytic decomposition, the operating parameters, such as, catalyst type, catalyst concentration, initial concentration of contaminant, and pH were studied. Furthermore, optimum parameters were applied to different contaminates.

**2.5 Parameters affecting the photo catalytic process**

Different factors affect the photo catalytic process were studied. Optimizing chemical composition was the first one. It was a start point for further investigations according to different experimental conditions (photolysis/photo-catalysis). Moreover, the impact of thermal treatment of the photo catalyst on the photo catalytic process was examined. The optimum photo catalyst was examined under other parameters such as pH, catalyst loading, and initial concentration. Furthermore, the photo catalytic activity against different organic contaminates was investigated.

To examine the influences of the \( \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticles loading on the photo catalytic process of CR, experiments were conducted using diverse concentrations of \( \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) varying from 200 to 500 mg/l,
using the same initial concentration of the CR under same experimental conditions.

Three values for pH were considered, covering the pH rage (5,7 and 9). The pH of the dye solution in the presence study is adjusted using HNO₃ (for lower pH) and NaOH (for higher pH).

3-RESULTS AND DISCUSSION

3.1 PHOTOCATALYTIC POTENTIAL OF NiₓZn(1-x)Fe₂O₄ NANOPIRTICLES

CR is a typical and the first anionic synthetic dye, which has two azo (–N=N–) chromophore [Di Paolaa et al; 2012]. Like other azo dyes, it is very stable because of its complex aromatic structure; it is not easily degradable. The stability of CR in water (hydrolysis) and under the exposure to UV radiation (photolysis) was examined. Figure (3) shows the degradation profile of 40 ppm CR in water with UV exposure for 3h. It was obvious that there is no significant degradation of CR in water, which was expected and confirmed regarding the employed CR concentration. Furthermore, photolysis of CR was also negligible since the produced OH• and H• radicals were not effective in UV-oxidation processes without suitable ferrite catalyst.

3.2 EFFECT OF CATALYST CONCENTRATION

Figure (4) shows the photo catalytic profiles for different concentrations of Ni₀.5Zn₀.5Fe₂O₄. It shows that the increase of photo degradation with relative increasing of concentration Ni₀.5Zn₀.5Fe₂O₄ for 40 ppm CR. Increasing
the concentration of Ni₀.₅Zn₀.₅Fe₂O₄ enhances photo degradation rate, which may be attributed to increasing the rate formation of hydroxyl radical due to the photo catalytic behaviour of Ni₀.₅Zn₀.₅Fe₂O₄. Which is mainly responsible for dye degradation of the existing contaminant. The overall photo degradation potentials for the 400 ppm and 500 ppm concentrations of the nano catalyst are very close. Therefore, it was convenient to select the 400 ppm concentration for further analysis.

3.3 EFFECT OF pH

In addition, exploring if Ni₀.₅Zn₀.₅Fe₂O₄ photocatalyst could be applied for a broad pH range.

Figure (5) represent the effect of pH on photo catalytic removal profiles of 40 ppm CR by 400ppm Ni₀.₅Zn₀.₅Fe₂O₄ nanoparticles at ambient temperature 25°C. Obviously, the maximum removal of CR achieved at pH 6, which could be attributed to relatively increase in H⁺ ion concentration in the system with respect to higher pH values. Low pH leads to the surface of the Ni₀.₅Zn₀.₅Fe₂O₄ nanoparticles acquires a positive charge by absorbing H⁺ ions. Hereafter, the surface turn into positively charged at low pH, a meaning fully robust electrostatic attraction developed between the positively charged surfaces of Ni₀.₅Zn₀.₅Fe₂O₄ and CR molecule, leading to maximum adsorption of dye. As the pH of the system rises, the number of negatively charged spot rises and the number of positively charged spots declines. A negatively charged surface spot on the Ni₀.₅Zn₀.₅Fe₂O₄ nanoparticles does not prefer the adsorption an anionic dye molecule such as CR, due to the
electrostatic repulsion. On the other hand, the photo catalytic degradation of CR did not affect significantly with respect to pH. Even, the relatively highest photo catalytic performance was also observed at pH 6. It is obviously that photo catalytic degradation of CR could be carried out successfully over a pH band form 6-10. The pH affects not only surface properties of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles but also the dissociation of dye molecule and the formation of the hydroxyl radical. The decrease in CR degradation under alkaline condition attributed to the negative charge surface of ferrite because of the increase concentration of OH- radical, thereby repelling the dye molecule.

4-CONCLUSION

In summary, Photo degradation of Congo red in aqueous solutions with synthesized Ni/Zn ferrites was studied. The effects of amount of Nano Ni/Zn ferrites. The extreme photo catalytic effectiveness was achieved by Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$, it succeeded to eliminate about 97% of 40ppm CR after 3h. Photo catalytic degradation of CR could be carried out successfully over a pH band form 6-10. The pH affects not only surface properties of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$

nanoparticles but also the dissociation of dye molecule and the formation of the hydroxyl radical.
(1) List of chemicals

| NO | CHEMICALS               | CHEMICAL FORMULA     | PURITY / GRADE | SUPPLIER                  |
|----|-------------------------|----------------------|----------------|----------------------------|
| 1  | Ferric sulfate penta hydrate | Fe₂(SO₄)₃·5H₂O | 98% RG         | MERCK (Germany)            |
| 2  | Nickel sulfate           | Ni₃(SO₄)            | 99% RG         | MERCK (Germany)            |
| 3  | Zinc sulfate hepta hydrate | Zn(SO₄)·7H₂O | 99.5% RG       | MERCK (Germany)            |
| 4  | Sodium Hydroxide pellets | NaOH                | 98 % RG        | MERCK (Germany)            |
| 5  | Acetone                  | C₃H₆O               | 99% RG         | MERCK (Germany)            |
| 6  | Chlorpyrifos             | C₉H₁₁Cl₃NO₅PS      | 95% Technically | K.Z (Egypt)                |
| 7  | Malathion                | C₁₀H₁₉O₄PS₂         | 95% Technically | N.C.I.C (Egypt)            |
| 8  | Congo Red                | C₃₂H₃₂N₆Na₆O₁₀S₂    | ≥97.0% Analytical Standard | Sigma-Aldrich (USA)       |
| 9  | Ethanol                  | C₂H₅OH              | Absolute       | Sigma-Aldrich (USA)       |
FIGURES

**Figure (1):** Congo red Structural Formula

**Figure (2):** the photochemical cell used in the photo catalytic process
Figure (3) Stability of CR in aqueous solution with UV at pH6 and ambient temperature 25°C

Figure (4): The Effect of mass concentrations of Ni_{0.5}Zn_{0.5}Fe_{2}O_{4} nanoparticles on photocatalytic removal profile of CR(40ppm) in duration time of 3h at pH6 and ambient temperature 25°C.
Figure (5): Effect of pH on removal profile of 40 ppm Congo red by 400 ppm Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles at ambient temperature 25°C

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استخدام البنيسل-زنك فيز في إزالة صبغة أحمر الكونغو

مصطفى

تستخدم صبغة أحمر الكونغو العضوية كنموذج للملوثات العضوية للمياه، وفي هذه الورقة البحثية يتم استخدام جزيئات الحديد النانوية المحضره في تفكيك وإزالة صبغة أحمر الكونغو تحت تأثير عوامل مختلفة كالاس الهيدروجيني (pH)، وتكترظ بمعنفة من Ni$_x$Zn$_x$Fe$_2$O$_4$، وتركز مختارة من Ni$_x$Zn$_x$Fe$_2$O$_4$ مع حلول مصغرة تحت ضوء الشمس في إزالة صبغة أحمر الكونغو في وجود Ni$_x$Zn$_x$Fe$_2$O$_4$ كعامل حماية بحيث نجحت الطريقة في إزالة 97% من 40 جزء في المليون من الصبغة خلال 3 ساعات. تم أجراء التحلل الضوئي التحفيزي في نطاق الأس الهيدروجيني (6–10)، ووجد أن الأس الهيدروجيني لا يؤثر على الخصائص السطحية للجسيمات النانوية Ni$_x$Zn$_x$Fe$_2$O$_4$. فحسب، بل يؤثر أيضا على تفكك جزيئات الصبغة وتكوين شقوق الهيدروكسيل.

كلمات مفتاحية: صبغة أحمر الكونغو، طريقه التحلل الضوئي، Ni$_x$Zn$_x$Fe$_2$O$_4$. 

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