

THE USE OF $\text{Ni}_x\text{Zn}_x\text{Fe}_2\text{O}_4$ 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 $\text{Ni}_x\text{Zn}_x\text{Fe}_2\text{O}_4$ concentrations. The results show that Congo red (CR) removal was succeeded using photo degradation method in the presence of $\text{Ni}_x\text{Zn}_x\text{Fe}_2\text{O}_4$ 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 $\text{Ni}_x\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoparticles but also the dissociation of dye molecule and the formation of the hydroxyl radical.

Keywords: $\text{Ni}_x\text{Zn}_x\text{Fe}_2\text{O}_4$, 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].

$\text{Ni}_x\text{Zn}_x\text{Fe}_2\text{O}_4$ is used in hardness natural organic compounds and alkalinity removal, decolorisation of pulp mill effluent and desalination [Chenga et al; 2015]. After adsorption, $\text{Ni}_x\text{Zn}_x\text{Fe}_2\text{O}_4$ can be removed from the medium by a magnet. It is a nontoxic, scalable economic and efficient method. Synthesis of $\text{Ni}_x\text{Zn}_x\text{Fe}_2\text{O}_4$ 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 $Zn_xNi_{(1-x)}Fe_2O_4$ 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, $Fe(NO_3)_3 \cdot 9H_2O$, nickel(II) nitrate, $Ni(NO_3)_2 \cdot 6H_2O$, and zinc nitrate, $Zn(NO_3)_2 \cdot 6H_2O$ 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.[Peternele *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 synthesized Nano ferrite. 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 range (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 Ni_xZn_(1-x)Fe₂O₄ NANOPARTICLES

CR is a typical and the first anionic synthetic dye, which has two azo (–N=N–) chromophore [Di Paola 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 Ni_{0.5}Zn_{0.5}Fe₂O₄. It shows that the increase of photo degradation with relative increasing of concentration Ni_{0.5}Zn_{0.5}Fe₂O₄ for 40 ppm CR. Increasing

the concentration of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ enhances photo degradation rate, which may be attributed to increasing the rate formation of hydroxyl radical due to the photo catalytic behaviour of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. 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 $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ 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 $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ 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 $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ 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 $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ 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 $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ 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 $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ 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 $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, 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 $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$

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	$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$	98% RG	MERCK (Germany)
2	Nickel sulfate	$\text{Ni}_2(\text{SO}_4)$	99% RG	MERCK (Germany)
3	Zinc sulfate hepta hydrate	$\text{Zn}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$	99.5% RG	MERCK (Germany)
4	Sodium Hydroxide pellets	NaOH	98 % RG	MERCK (Germany)
5	Acetone	$\text{C}_3\text{H}_6\text{O}$	99% RG	MERCK (Germany)
6	Chlorpyrifos	$\text{C}_9\text{H}_{11}\text{Cl}_3\text{NO}_3\text{PS}$	95% Technically	K.Z (Egypt)
7	Malathion	$\text{C}_{10}\text{H}_{29}\text{O}_6\text{PS}_2$	95% Technically	N.C.I.C (Egypt)
8	Congo Red	$\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$	$\geq 97.0\%$ Analytical Standard	Sigma-Aldrich (USA)
9	Ethanol	$\text{C}_2\text{H}_5\text{OH}$	Absolute	Sigma-Aldrich (USA)

FIGURES

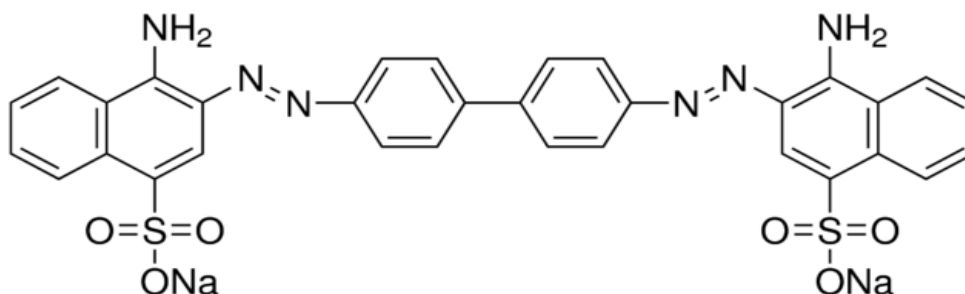


Figure (1): Congo red Structural Formula

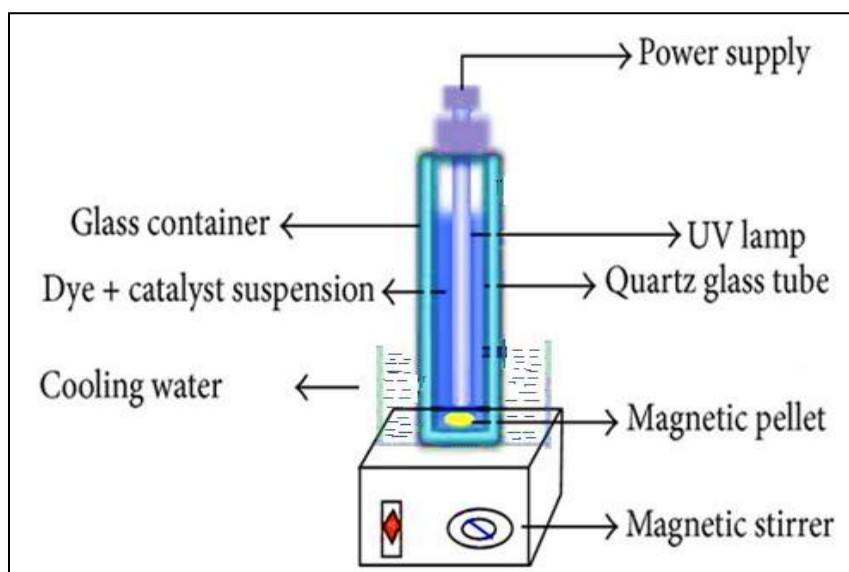


Figure (2): the photochemical cell used in the photo catalytic process

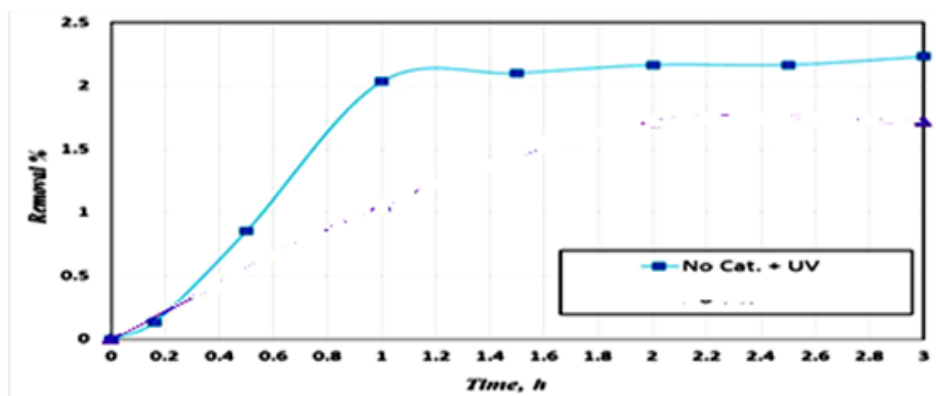


Figure (3) Stability of CR in aqueous solution with UV at pH6 and ambient temperature 25°C

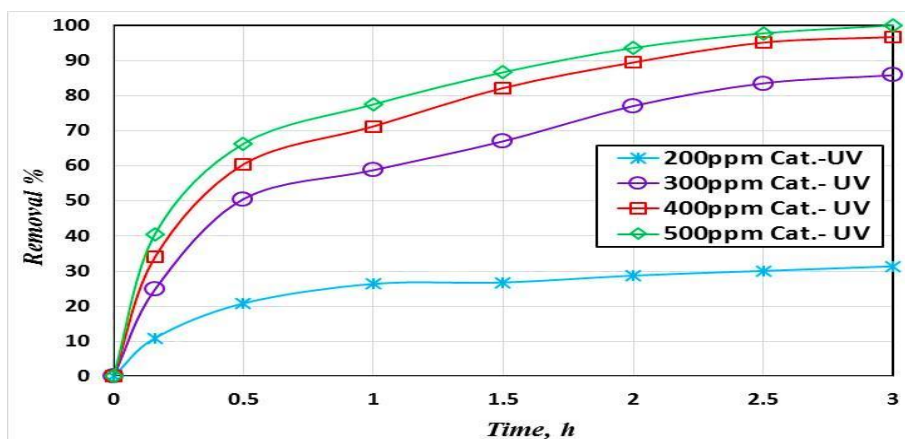


Figure (4): The Effect of mass concentrations of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles on photocatalytic removal profile of CR(40ppm) in duration time of 3h at pH6 and ambient temperature 25°C.

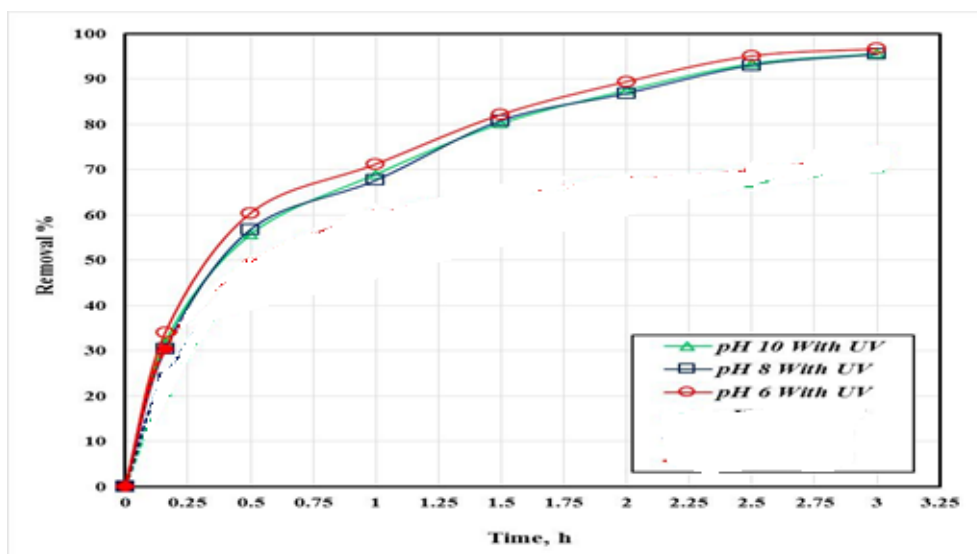


Figure (5): Effect of pH on removal profile of 40 ppm Congo red by 400ppm $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles at ambient temperature 25°C

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استخدام النيكول-زنك فيريت في إزالة صبغة أحمر الكونغو

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المستخلص

تستخدم صبغة احمر الكونغو العضويه كنموذج للملوثات العضويه للمياه، وفي هذه الورقه البحثيه يتم استخدام جزيئات الحديد النانويه المحضره في تفكيك وازاله صبغه احمر الكونغو تحت تأثير عوامل مختلفه كالاس الهيدروجيني (pH) ، وتركيزات مختلفه من Ni_xZn_xFe₂O₄. اظهرت النتائج نجاح طريقه التحلل الضوئي التحفيزي في ازاله صبغه احمر الكونغو في وجود Ni_xZn_xFe₂O₄ كعامل حفاز، حيث نجحت الطريقه في ازاله ٩٧% من ٤٠ جزء في المليون من الصبغه خلال ٣ ساعات. تم اجراء التحلل الضوئي التحفيزي في نطاق الاس الهيدروجيني (٦-١٠)، ووجد ان الاس الهيدروجيني لايؤثر علي الخصائص السطحيه للجسيمات النانويه Ni_xZn_xFe₂O₄، فحسب، بل يؤثر ايضا علي تفكك جزيئات الصبغه وتكوين شقوق الهيدروكسيل. كلمات مفتاحيه: صبغه احمر الكونغو ، طريقه التحلل الضوئي ، Ni_xZn_xFe₂O₄.