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## Neutral red removal Using different techniques: Direct photolysis, UV/H<sub>2</sub>O<sub>2</sub>, Fenton and Photo-Fenton

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### ABSTRACT

In this study, evaluation and comparison of the effectiveness of some photochemical systems such as direct UV photolysis, H<sub>2</sub>O<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> (Fenton process) and H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>/UV (Photo-Fenton process) have been investigated in lab-scale experiments to remove Neutral Red (abbreviated as NR) from aqueous solutions. From the experimental results, it has been found that color removal followed the increasing order: Direct UV photolysis < H<sub>2</sub>O<sub>2</sub>/UV < H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> < H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>/UV.

**Keywords:** Photolysis; Photo-Fenton process; Fenton process; Removal efficiency; Neutral Red

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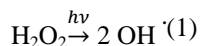
### INTRODUCTION

Some chemicals released into the environment in the course of different applications can become persistent hazardous, threatening not only to human health but to the entire ecosystem (Kasturyetal. 2015). Neutral red (NR; 3-amino-7-dimethylamino-2-methyl phenazine) is a synthetic phenazine that has found a wide range of applications in multiple disciplines for over a century. It is a tricyclic aromatic amine containing two nitrogen atoms in the aromatic ring structure. The presence of a C–N substitution in aromatic compounds, including that found in NR, permits NR to be water soluble and therefore increasing its bioavailability (Kobeticovaetal. 2011). This may result in increasing mobility of NR, potentially increasing its toxicity and mutagenicity (Kasturyetal., 2015). Since its earliest known use as a vital stain in 1894 [Koehring, 1930], NR has been broadly used as an intracellular pH indicator (Lamannaa and McCracken, 1984), ecological marker (New, 1958), textile dye (Sharma etal. 2009; Zhou, 2001; Guerard etal. 2012), histological stain in cytotoxicity assays (Guerard etal., 2012) and recently as electron shuttles in microbial fuel cells for electricity generation [Park and Zeikus, 2000] and during reductive hemolytic ons (Watanabe etal., 2009)

In this fact, treatment of aqueous solution containing NR by advanced oxidation process is very interesting. In this system, the free radicals (·OH) which are responsible for the degradation of organic pollutants into biodegradable compounds or complete mineralization into CO<sub>2</sub>, H<sub>2</sub>O and inorganic ions (Yee etal., 2010; Dias etal., 2014) (Dias et al., 2014). The use of Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> as an oxidant for wastewater treatment is attractive since iron is highly abundant and non-toxic, and a 30% hydrogen peroxide aqueous solution is easy to handle and environmentally not harmful.

Nevertheless, the efficiency of the Fenton process is strongly dependent of pH; the optimum pH value is around 3 (Jaafar and Boussaoud, 2014).

The H<sub>2</sub>O<sub>2</sub>/UV process occurs upon irradiation of the pollutant solution containing H<sub>2</sub>O<sub>2</sub> with UV light. This causes the hemolytic cleavage of H<sub>2</sub>O<sub>2</sub>. The main reaction of H<sub>2</sub>O<sub>2</sub>/UV is given below (Eq. (1)):(Andreozzi *et al.*, 1999; Pignatello *et al.*, 2006).



The aim of this research paper is to evaluate and to compare the effectiveness of some advanced oxidation processes such as direct UV photolysis, UV/H<sub>2</sub>O<sub>2</sub>, Fenton and Photo Fenton process, on the removal of NR from an aqueous solution.

## MATERIALS AND METHODS

### 2.1. Materials

Neutral Red (a basic dye of phenazine type (C.I. No 50040)) was obtained from REACTIFS RAL (RHON POULLENC), the molecular structure of it is displayed in Fig. 1. Hydrogen peroxide (110 volumes) was obtained from Scharlau, ferrous sulfate (FeSO<sub>4</sub>.7H<sub>2</sub>O), sulfuric acid and sodium hydroxide were all obtained from Loba Chemie. All chemicals were of analytical grade and were used without any further purification. Water used throughout was distilled water.

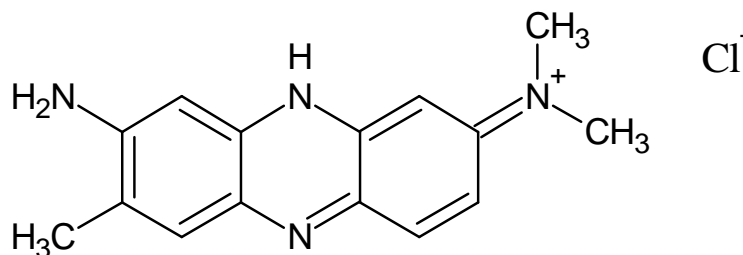


Figure 1: molecular structure of neutral Red

The concentration of the dye in the reaction mixture at different reaction times was determined by measuring the absorption intensity at  $\lambda_{\text{max}}=530$  nm using a UV-Vis spectrophotometer (RAYLEIGH UV-1800). The removal efficiency of NR was defined as follows:

$$\text{Removal efficiency (\%)} = (A_0 - A_i) / A_0 \times 100\% \quad (1)$$

Where  $A_0$  is the initial absorbency of NR, and  $A_i$  is the absorbency of NR at reaction specifically time.

### 2.2. Experimental methods

All experiments were carried out in a photochemical reaction instrument (Figure 2), which has 1000 mL beaker; and stirred by a magnetic stirrer. For the irradiation source, a plunging tube containing a low pressure mercury UV lamp (125 W, manufactured by Ingelec) was introduced in the solution. This tube had a quartz cylindrical jacket, in which water circulated to avoid the heating of the solution. Solution pH values were adjusted to the desired level using dilute sulfuric acid and sodium hydroxide, which were measured by a pH meter (CRISON):

**Direct photolysis procedure:** Solutions of NR were prepared and exposed to UV irradiation without any reagent.

**UV/H<sub>2</sub>O<sub>2</sub> system procedure:** Each experimental run was performed by taking proper amount of dye solution followed by the addition of hydrogen peroxide. The reactions were initiated by UV irradiation.

**Fenton procedure:** Each experimental run was performed by taking proper amount of dye solution followed by the addition of ferrous ion and dilution with distilled water. The reactions were initiated by adding hydrogen peroxide to the reaction beaker



Figure 2: photochemical reaction instrument

**Photo-Fenton procedure:** The same Fenton procedure but the reaction beaker was exposed to UV irradiation.

The dye taken samples were taken out from the beaker periodically using a pipette and were immediately analyzed. Each experiment was replicated three times.

## RESULTS AND DISCUSSION

### 3.1. UV-vis spectrum of NR

The UV-vis spectrum of NR in natural pH (6.25) and in dilute concentration was recorded from 200 to 800 nm using a UV-vis spectrophotometer with a spectrometric quartz cell (1 cm path length). Fig. 3 shows that this compound exhibits an intense band located around 266 nm (UV region) and another one at around 530 nm (visible region).

The pH affected the behavior of the dye, mainly in basic medium (pH 9). Indeed, we observe a color change of the solution (turning into yellow). This color change can be due to the deprotonation process. Besides, we observe the change in band position from 530 to 428 nm. By contrast, we remark no change in color and also in band positions in acidic medium (pH = 3). From the spectrums of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  in 500–600 nm have not absorption (Jaafar *et al.*, 2016).

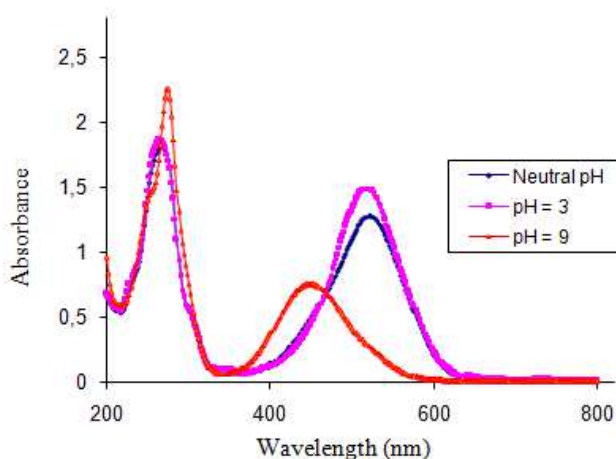


Figure 3. Spectrum of NR. Influence of pH.

### 3.2. Comparative experiments

Comparative experiments were undertaken in the presence of (Fig. 4) (i) Direct UV photolysis (ii)  $\text{H}_2\text{O}_2$ /UV Process (iii) Fenton Process (iv) Photo-Fenton process.

In our case, the different processes were carried out at room temperature, with an initial concentration of NR of 0.156 mM. Hydrogen peroxide was added at a  $[\text{H}_2\text{O}_2]/[\text{NR}]$  molar ratio of approximately 5 ( $\text{H}_2\text{O}_2$ /UV process,

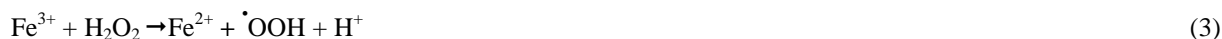
Fenton process and photo-Fenton process). The initial concentration of  $\text{Fe}^{2+}$  ions was 0.072mM (Fenton process and photo-Fenton process). These optimum conditions were determined in other study (Jaafaretal., 2016).

**Table 1: Initial rate of different systems**

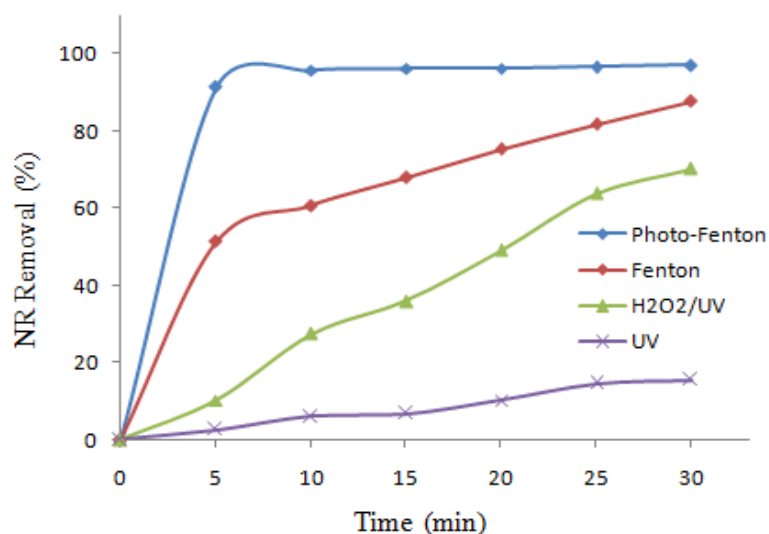
Process	Initial rate $r_0$ (mM min <sup>-1</sup> )
UV	0.0008
H <sub>2</sub> O <sub>2</sub> /UV	0.0032
Fenton	0.016
Photo-Fenton	0.0285

From the experimental results, in direct UV photolysis, Fig. 4 presents low NR removal efficiency (only 15%). The reason is the low absorbance of light by NR. For other processes the NR removal efficiency increased and follow the ascending order for a reaction time of 30 min: H<sub>2</sub>O<sub>2</sub>/UV (70%) < Fenton (87%) < Photo-fenton ( 97%). This can be attributed to the increased production of more •OH radicals in these systems respectively.

The rate of NR removal could be increased by irradiation of Fenton with UV light (photo-Fenton process). UV light leads not only to the formation of additional hydroxyl radicals advanced oxidation process but also to recycling of ferrous catalyst by reduction of  $\text{Fe}^{3+}$ (Eq. 2). In this way, the concentration of  $\text{Fe}^{2+}$  is increased and the overall reaction is accelerated (Modrishahla etal., 2007).



Furthermore, the removal initial rate constant of the dye for different systems was calculated (Tab. 1). It is clear that  $r_0$  (Photo-Fenton) >  $r_0$  (Fenton) >  $r_0$  (H<sub>2</sub>O<sub>2</sub>/UV) >  $r_0$  (UV).



**Figure 4.**Effect of various processes on NR removal (%). Reaction conditions: initial concentration of NR,  $[\text{NR}]_0 = 0.156\text{mM}$ , initial concentration of hydrogen peroxide,  $[\text{H}_2\text{O}_2]_0 = 0.750\text{mM}$ , initial concentration of Ferrous sulfate,  $[\text{Fe}^{2+}]_0 = 0.072\text{mM}$ , initial pH = 3 and room temperature.

## CONCLUSION

This study represent the performance and the comparison of different systems to removal NR ( $1.56 \times 10^{-4}\text{M}$ ) from an aqueous solution. Experiments conducted on one side by direct UV photolysis, on the other side by H<sub>2</sub>O<sub>2</sub>/UV, Fenton process and Photo-Fenton process were achieved. Based on the experimental results presented above, it has been found that Photo-Fenton process was powerful method for decolorization of NR. Moreover, the initial removal rates of NR were determined.

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