

FACTORS INFLUENCING THE PHOTOCATALYTIC DECOLORIZATION OF METHYLENE BLUE IN THE PRESENCE OF NATURAL IRON OXIDE AND OXALIC ACID UNDER UV IRRADIATION.

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Abstract

In this work, the methylene blue (MB) heterogeneous photodegradation was investigated in the natural iron oxide (NIO) and oxalic acid process under UV irradiation. The adsorption of MB onto the surface of NIO was found favorable by the Langmuir approach. Under the operating conditions of this study, the photo-Fenton reaction was set up in co-presence of NIO and Oxalic Acid (OA). Where, the total degradation of MB was achieved in 90 min. The mechanism of MB photodegradation was discussed and the use of 2.0 % of tertibutanol as a scavenger of ·OH confirmed their intervention in the reaction. The effect of oxygen and hydrogen peroxide were investigated, the results demonstrated that the oxygen was necessary in the MB photodegradation and that the optimum concentration of hydrogen peroxide was found to be 5×10^{-4} M. measuring the chemical oxygen demand (COD) demonstrates the effectiveness of our natural iron oxide in the degradation of organic pollutants.

Keywords: Photodegradation; Iron oxide; Oxalic acid; Methylene Blue; Adsorption.

Résumé

Dans ce travail, la photodégradation hétérogène du bleu de méthylène (BM) a été étudiée en présence de l'oxyde de fer et de l'acide oxalique sous irradiation ultra-violette. L'isotherme de Langmuir décrit l'adsorption du BM sur la surface de l'oxyde de fer. En coprésence de l'oxyde de fer naturel et de l'acide oxalique, la réaction de photo-Fenton a été mise en place et la dégradation totale du BM a été obtenue au bout de 90 minutes. L'ajout de 2% du tertibutanol comme inhibiteur des radicaux hydroxyles (·OH) confirme son implication dans la réaction. Les résultats montrent aussi que l'oxygène est important au processus de photodégradation du BM et que la concentration optimale du peroxyde d'hydrogène est égale à 5×10^{-4} M. la mesure de la demande chimique en oxygène (DCO) montre bien l'efficacité de notre oxyde de fer naturel dans le processus de dégradation de polluants organiques.

Mots clés: Photodégradation; Oxyde de fer; Acide oxalique; Bleu de méthylène; Adsorption.

ملخص

في هذا العمل، قمنا بدراسة التفكك الإشعاعي لأزرق الميثيلان بوجود أكسيد الحديد و حمض الأوكسليك تحت الأشعة فوق البنفسجية، إمتزاز أزرق الميثيلان على سطح أكسيد الحديد يتبع نظام Langmuir. عند تواجد حمض الأوكسليك و أكسيد الحديد معاً، تشكل نظام photoFenton وتم التفكيك الكلي لأزرق الميثيلان في 90 دقيقة. إضافة 2% من tertibutanol يؤكد أن الجذور الهيدروكسيلية هي المسؤولة على التفاعل. أثبتت النتائج ضرورة الأوكسجين في التفاعل وأن ماء الأوكسجين مسرع لتفكك أزرق الميثيلان عند تركيز 5×10^{-4} مول/ل. متابعة تفاعل تفكك أزرق الميثيلان بواسطة الطلب على الأوكسجين الكيماوي برهن فعالية أكسيد الحديد

الكلمات المفتاحية: التفكك الإشعاعي، أكسيد الحديد، حمض الأوكسليك، أزرق الميثيلان، الإمتزاز.

1- Introduction

Dyes are used widely in textile, plastic, dyeing, paper, printing, pharmaceutical and cosmetic industries [1]. Dye effluents from different industries may contain chemicals that exhibit carcinogenicity, reproductive and developmental toxicity, as well as neurotoxicity and chronic toxicity toward humans and animals [2,3]. In general, the dyes used by industries have good stability, most of which are recalcitrant to light, oxidation and aerobic digestion.

Conventionally, the dyes wastewater can be treated by biological, physical and chemical methods [4-6]. Biological treatment processes are often ineffective in removing dyes which are highly structured polymers with low biodegradability [7,8]. Furthermore, the majority of dyes is only adsorbed on the sludge and is not degraded [9]. Various physicochemical techniques, such as chemical coagulation, adsorption on active carbon, reverse osmosis and ultrafiltration [4], are usually used to treat the wastewater contained dyes. But these methods are only available to the lower dye concentrations and they are non-destructive, since they just transfer organic compounds from water to another phase, thus causing secondary pollution. Consequently, regeneration of the adsorbent materials and post-treatment of solid-wastes, which are expensive operations, are needed [10]. Chlorination and ozonation are also being used for the removal of certain dyes but at slower rates as they have often high operating costs and limited effect on carbon content [11].

Advanced oxidation processes (AOPs) that rely on the highly reactive oxidant, hydroxyl radical ($\cdot\text{OH}$), can be used as alternative technologies for the treatment of wastewater contaminated by dyes. Over the past decade, the various Fenton systems were developed; the heterogeneous systems using iron oxides have an advantage over the homogeneous systems, in that the separation of catalysts after the treatment is simple.

In nature, iron, oxalic acid and sunlight can establish a homogeneous photo-Fenton-like system where iron exists in a dissolved form or a heterogeneous photo-Fenton-like system where iron is in a solid form. The heterogeneous Fe(III)-oxalate system should be more applicable to the natural environment, because the iron species are mostly present as amorphous or (hydr)oxides [12]. Many studies are reported on the photodegradation of pollutants in the presence of iron oxide and oxalic acid (heterogeneous system photo-Fenton) [13-15].

The aim of this work is to study the effectiveness natural Algerian iron oxide (NIO) in Methylene Blue (MB) photodegradation process in the presence oxalate. Firstly, the adsorption of MB onto NIO surface was investigated and Langmuir, Freundlich isotherms were studied. After that, the degradation of MB under UV irradiation was investigated. The effect of oxygen, hydrogen peroxide and tertio-butanol were illustrated. The mechanism of MB photodegradation by NIO-OA process was discussed.

2. Materials and methods

2.1. Materials

Methylene Blue was purchased from Reidel-de Haën (purity greater than 99 %). The formula, molecular weight and maximum wavelength of light absorbed by MB were $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+\text{Cl}^-$, 385.19 $\text{g}\cdot\text{mol}^{-1}$ and 664 nm, respectively. The structure of RhB is shown in Fig 1. Oxalic acid (99.5 %) from Prolabo. The hydrogen peroxide (30 %) from (Prolabo). The natural iron oxide (NIO) was washed several times with distilled water and dried at 45 $^{\circ}\text{C}$.

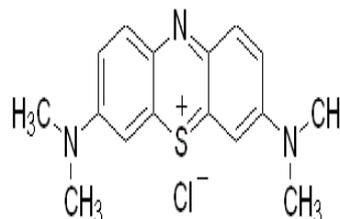


Fig.1. The molecular structure of methylene blue.

2.2. Procedure and analysis

The adsorption experiments were carried out, using 50 ml of MB solution, by varying the initial concentration of dye from 8×10^{-6} to 4×10^{-5} $\text{mol}\cdot\text{L}^{-1}$, catalyst loading 1 $\text{g}\cdot\text{L}^{-1}$ at natural pH (pH = 5.91) and 20 ± 1 $^{\circ}\text{C}$. The adsorption equilibrium took 30 min for the NIO.

The irradiation experiments were carried out with 50 ml of solution with a desired dye concentration and iron oxide loading at natural pH and 20 ± 1 $^{\circ}\text{C}$. During both dark adsorption and UV-irradiation periods, samples of 2 ml were collected at regular times and filtered on a Millipore filter, 0.45 μm prior to analysis. The concentration was monitored by measuring the absorbance at $\lambda_{\text{max}} = 664$ nm, using a UNICAM HELIOS α UV-visible spectrophotometer.

2.3. Characterization of iron oxide

The natural iron oxide was characterized by X-ray diffraction in order to determine the crystal phase composition; by the Brunauer–Emmett–Teller (BET) method to identify the total surface area and total pore volume and the chemical composition was determined using X-ray Fluorescence. The results of detailed analysis were shown in previous study of our group [16]. Which the X-ray pattern has showed 9 characteristics peaks of hematite. The results of BET show that the NIO has the surface area equal to 79.015 m².g⁻¹ and total pore volume 0.0892 cm³ g⁻¹.

3. Results and discussion

3.1. Adsorption isotherm

It is likely that sorption of the dye is an important parameter in determining photocatalytic degradation rate. Dark adsorption was performed to evaluate the adsorption of MB onto the iron oxide. In this study two isotherms, Langmuir and Freundlich isotherms have been selected to evaluate the adsorption capacity of the natural iron oxide. The expression of the Langmuir model [17,18] is:

$$Q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \quad (1)$$

The linear transformation of Eq.(1) can be expressed by the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}} \quad (2)$$

The Freundlich model is an empirical equation that assumes heterogeneous adsorption due to the diversity of adsorption sites [19,20]. The Freundlich equation is:

$$Q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

The linear transformation of Eq. (3) can be expressed by the following equation:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

Where Q_e is the amount of dye adsorbed per gram of iron oxide (mg.g⁻¹); C_e denotes the equilibrium concentration of dye in solution (mol.L⁻¹); K_L represents the Langmuir constant (mol.L⁻¹) that relates to the affinity of binding sites and Q_m the theoretical saturation capacity of the monolayer (mol.L⁻¹). K_f and n are the Freundlich constants (Table 1).

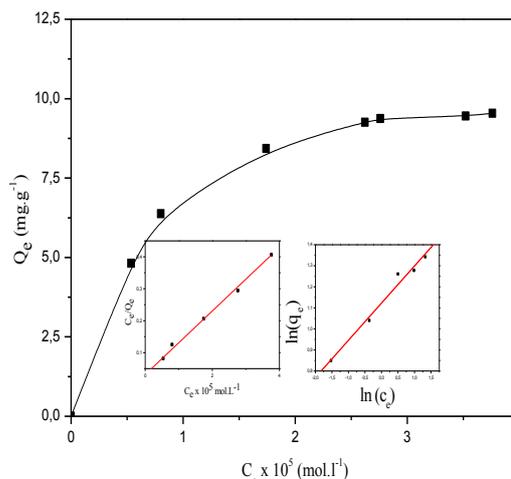


Fig.2. The adsorption isotherm of MB on the surface of NIO obtained by plotting the equilibrium concentration (C_e) vs the adsorbed amounts of MB (Q_e).

The adsorption isotherm $Q_e = f(C_e)$ for NIO catalyst are shown in Fig. 2, indicating that the Langmuir model is applicable for L-shape type according to the classification of Giles et al [21]. L-shape type of the isotherm means that there is no strong competition between the solvent and the adsorbate to occupy the adsorbent surface sites. Experimental results present a good correlation of the Langmuir model with R^2 above 0.998. This indicates a unique adsorption sites, uniform monolayer adsorption and no interaction between the adsorption sites. It appears that the adsorption coverage is small for iron oxide exhibit the higher adsorption constant and adsorbed quantity.

Table 1: Summarized the coefficients of the Langmuir and Freundlich isotherms.

	$Q_{max} \times 10^{-6}$ mg.g ⁻¹	$k_L \times 10^5$ L.mg ⁻¹	R^2
Langmuir	11.28	1.56	0.998
	K_f	n	R^2
Freundlich	6.477	2.93	0.967

3.2. MB photodegradation in the presence of NIO

In order to illustrate the photochemical behavior of MB in OA/NIO/UV system, firstly, the direct photolysis of MB (irradiation without NIO and OA) was investigated ($[MB] = 10^{-5}$ mol.L⁻¹, $\lambda = [300-450$ nm], pH = 5.91, T= 20°C). Then, the reaction between OA and MB was studied in the dark and under irradiation ($[OA] = 4$ mM, $[MB] = 10^{-5}$ mol.L⁻¹). As show in Fig.3 in the presence of OA, the concentration of MB remained unchanged in the dark.

However, under irradiation, 44 % of MB was degraded. On the other hand, the direct photolysis of MB conducted to a weak efficiency 20 % of decolorization after 2 hours. Further, the total elimination of MB was achieved in NIO/OA/UV system at 90 minutes of irradiation. The results indicate that the combination of iron oxide, oxalate, and UV light is essential for MB photodegradation.

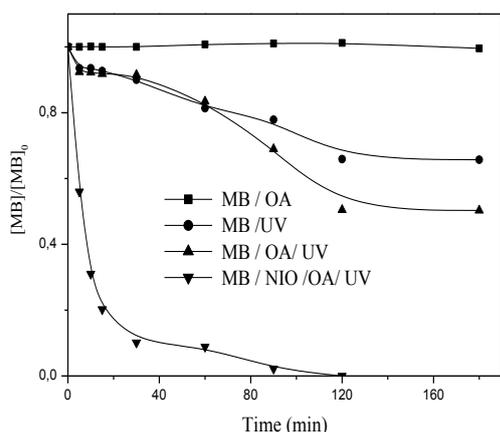
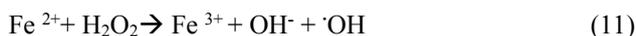
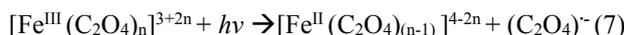
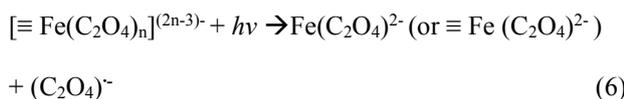


Fig.3. Photodegradation of MB (10^{-5} M) in different systems under UV irradiation ($[NIO] = 1 \text{ g.L}^{-1}$, $[OA] = 4 \text{ mM}$).

3.2.1. Mechanism of MB photodegradation process

Many authors have previously been described the main of hydroxyl radicals ($\bullet\text{OH}$) production in photochemical process in the co-presence of iron oxide and oxalate [12,14,22-24]. The oxalic acid form the complex with iron oxide on the surface $[\text{Fe(III)}(\text{C}_2\text{O}_4)_n]^{(2n-3)-}$ and in solution $[\text{Fe(III)}(\text{C}_2\text{O}_4)_n]^{(2n-3)-}$ (Eq.5), under radiation this complex can be excited to give the oxalate radical $(\text{C}_2\text{O}_4)^{\bullet-}$ (Eq. 6-7). After, many reactions were happened to create the photo-Fenton system and generate the hydroxyl radicals ($\bullet\text{OH}$) (Eq. 8-12).



3.2.2. Contribution of hydroxyl radical in photochemical process

To illustrate the intervention of hydroxyl radicals in the MB photodegradation mechanism, 2 % of tertibutanol was added as a scavenger of $\bullet\text{OH}$ to NIO-OA-MB suspension ($[NIO] = 1 \text{ g.L}^{-1}$, $[OA] = 4 \text{ mM}$, $[MB] = 10^{-5} \text{ M}$). Fig. 4 shows the total inhibition of MB photodegradation in the presence of tertibutanol, confirming that the hydroxyl radicals are the entities responsible on the MB photodegradation [16].

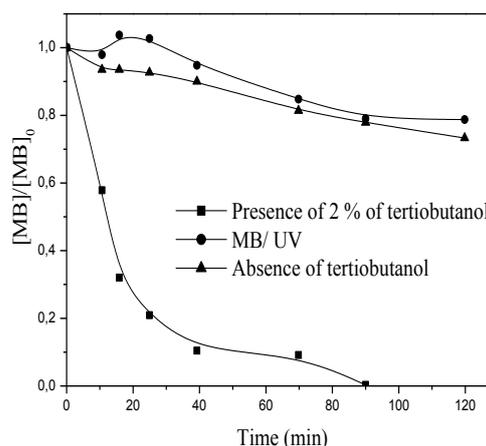


Fig.4. The effect of tertibutanol onto MB photodegradation in NIO/OA/UV process.

3.2.3. Effect of oxygen

In order to study the effect of oxygen on the MB photodegradation in the presence of NIO and OA, NIO/OA/MB suspension (1 g.L^{-1} , $4 \times 10^{-3} \text{ M}$ and $10^{-5} \text{ mol.L}^{-1}$) was irradiated at 365 nm in deoxygenated (nitrogen bubbling) and aerated system. The obtained results are represented in Fig. 5.

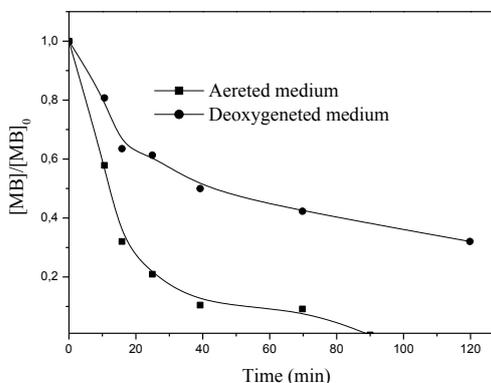


Fig.5. Kinetics of MB (10^{-5} M) disappearance under irradiation of deoxygenated and aerated system in presence of 1.0 g L^{-1} NIO and $4 \times 10^{-3} \text{ M}$ oxalic acid.

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As can be seen in fig (5), the MB photodegradation was slower in the deoxygenated system compared to the aerated system, because the oxygen is necessary to form hydrogen peroxide (Eq.8), which is responsible on hydroxyl radicals formation in photo-Fenton system [25].

3.2.4. Effect of hydrogen peroxide

The influence of the hydrogen peroxide concentration on the photodegradation kinetics of MB in the presence of iron oxide and oxalic acid was investigated using different concentration of H_2O_2 varying from 10^{-4} to 10^{-3} mol.L $^{-1}$. Fig 6 represents the variation of the apparent rate constant with the variation of the initial concentration of hydrogen peroxide.

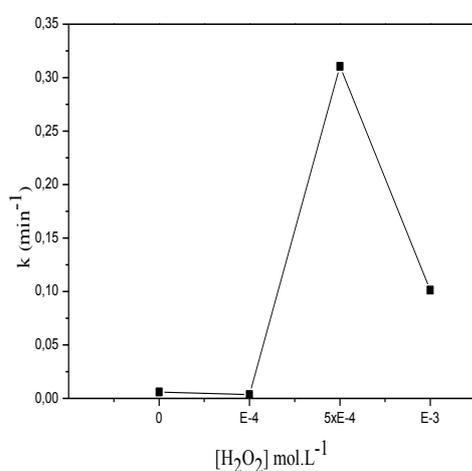
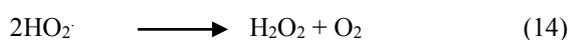
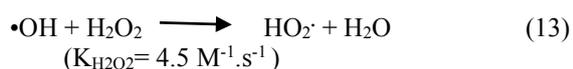


Fig.6. Effect of hydrogen peroxide concentration on the MB photodegradation by NIO/OA process ([MB]= 10^{-5} mol.L $^{-1}$, [NIO]= 1 g L $^{-1}$, [OA]= 4 mM) under UV irradiation.

The reaction rate of MB degradation was accelerated by increasing the concentration of hydrogen peroxide. Thus, more hydroxyl radicals were produced when the concentration of H_2O_2 was increased from 10^{-4} to 5.10^{-4} mol.L $^{-1}$. Nevertheless, further increase in the H_2O_2 concentration from 5.10^{-4} to 10^{-3} mol.L $^{-1}$ would result in the decrease of degradation of MB. This fact is due to the scavenging effect of hydroxyl radicals by hydrogen peroxide existing at high concentration (Eq.10).



The hydroperoxy radicals are predominantly produced in this case and they are much less reactive than hydroxyl radicals [26].

3.2.5. Chemical oxygen demand

The chemical oxygen demand test is widely used as an effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in terms of the total quantity of oxygen required for oxidation of organic matter to CO_2 and water. In order to have an idea of the toxicity of the photocatalyzed solution, their COD values were determined using the method presented by Thomas and Mazas [27]. The significant decrease in the COD values of methylene blue solution (from 127 to 18 mg/L) was observed and the variation of percentage of mineralization of methylene blue versus irradiation time is reported in Fig 7.

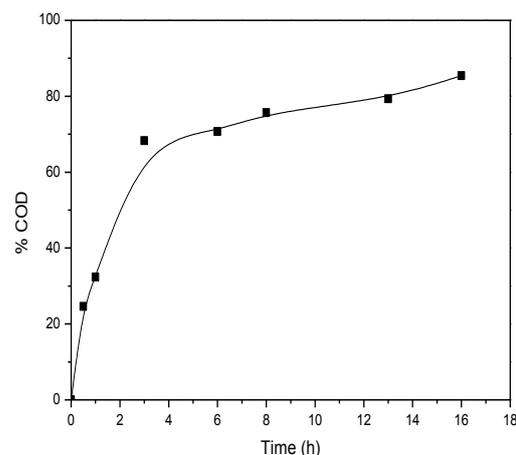


Fig.7. Variation the percentage of mineralization of MB (10^{-5} M) by NIO/OA/UV irradiation versus time.

From fig. 7, we can see that the COD percentage of methylene blue is equal to 85 %, this indicates the effectiveness of natural iron oxide in methylene blue photocatalytic degradation in the presence of oxalic acid.

4. Conclusion

The heterogeneous natural iron oxide–oxalate complex system, as a photo-Fenton-like system, was proven to be an effective method for the degradation of methylene blue.

The contribution of hydroxyl radicals has been proved by adding 2 % of tertio-butanol as a scavenger.

The oxygen has the important effect on the MB photodegradation process.

The decolorization of MB was enhanced by addition of low H_2O_2 dosage and retarded while over dosage was used, due to the formation of less reactive hydroperoxy radicals.

The COD measurement confirmed the effectiveness of natural iron oxide in degradation of methylene blue

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