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Photodegradation of Congo red and real textile industries effluent using natural Tunisian iron oxide

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ABSTRACT

Natural iron oxide as a low-cost, abundant and eco-friendly material has investigated in photo-Fenton process. In this study, two locally iron oxides were collected, prepared and characterized. X-ray diffraction (XRD), X-ray fluorescence (XRF), N_2 adsorption-desorption and UV-vis spectroscopy were used to investigate structural and optical properties of catalysts. Natural catalysts were used as photo-Fenton catalyst to investigate degradation rate of Congo red (CR) diazo dye under UV light irradiations and real textile industries effluent. Results show a total discoloration of CR within 45 min and a total mineralization within 60 min. Also, the treatment of real effluent is efficient by photo-Fenton process. Furthermore, stability of catalyst was evaluated and results show a good structural and chemical stability after several use of catalyst.

Keywords: Photo-Fenton; Natural iron oxide; Congo red; Degradation; Effluent textile; UV light

1. Introduction

Increasing agro-industrial activities cause a great pressure on the world's freshwater reserves. Very often, these activities generate a big diversity of chemicals products that can be discharged into natural streams and make a serious environmental problems [1]. Also, contamination of soil and groundwater by these organic chemicals imposes significant threats on water resources and public health. Some types of pollutants in water and soil are complex organic molecules which are difficult to biodegrade [2]. As a consequence, there is an increasing social pressure towards a sustainable use of water and a renewed interest in improving existing technologies for water treatment [3]. For this reason, several processes as physical, chemical and biophysical have been studied for their ability to destroy organic pollutants [4]. The conventional wastewater treatment technologies for these toxic compounds include biological treatment [5], chemical coagulation processes [6], adsorption by activated carbon [7], and the chemical processes [8]. However, many types of serious toxic pollutants such as dye are resistant to the biological treatment and the degradation way was very hard. Hence, common wastewater treatments cited previously present some inconvenient and negative effects. For examples, they are costly; a larger area is required for the degradation process and some process just transfer pollutant from water to solid that's required a further treatment.

Thus, a simple and efficient method can be applied to degrade the toxic dyes such as chemical oxidation that's considered as a powerful method for the remediation of wastewater [9]. Many oxidants such as peroxide, ozone and permanganate have employed and have been able to cause the complete chemical degradation of many toxic organic pollutants. Among chemicals oxidation processes the so called advanced oxidation processes (AOPs) was investigated and applied [10]. AOPs have been defined as those oxidation treatment based on the reaction of hydroxyl radical in an aqueous solution, it is a powerful and extremely reactive oxidant agent that can degrade organic pollutants efficiently [10–13]. Fenton process (Fenton reagent: (Fe^{2+}/H_2O_2)) is one of the most powerful oxidation used among AOPs [12,14]. It has been proved to be an efficient and attractive method for the removal of a large number

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of harmful and organic compounds [15–17]. However, this process is limited by the slurry system because, it produces a significant amount of iron sludge, which requires further separation and disposal [18], and also is less appropriate since it leads to high metal (iron or other transition metal) concentrations in the final effluent. So during these years, many researchers focused on the using of modified Fenton system, the so called Fenton-like system using heterogeneous catalyst and under UV light irradiations. In some research, iron solid mineral was used instead of soluble iron and it offers significant advantages in separation since in this case, the catalyst can be easily recovered by sedimentation or filtration and further used [19], and also, the reaction could be carried out at neutral pH.

Dye is one of the most common toxic pollutants in the natural environment over the world. Because, dye manufacturing industries and textile units dump toxic organic compounds to the nearer water courses leading to unpleasant consequences [20,21].

Congo red belongs to diazo dye class, which is widely used as a colorant in textile dyeing industries, as a histological stain for amyloid, as an indicator of pH [22]. It's cancerogenic and causes negatives effects in human health, and their biodegradation is difficult [23]. Many authors investigated Congo red degradation by different processes such as adsorption process using coal-activated carbon [24], heterogeneous Fenton-like oxidation using Al/Fe pillared clay [22], photocatalytic degradation by UV irradiated titania [25] , photodegradation under visible light irradiations using Fe° doped BiOCl as photocatalyst [26], photo-assisted Fenton using zero-valent metallic iron as a catalyst [27]. So, the removal of Congo red from waste waters is a challenging issue to protect human health and environment.

In this research, we investigate a heterogeneous photo-Fenton process to oxidize a model pollutant and real textile effluent, sampled from the output of textile industry, using two different natural catalysts collected from a local iron-ores deposit. UV light irradiations were chosen as energy source and Congo red as model pollutant because it is still extensively used worldwide in modern industry and daily life, and efficient treatment processes are needed. We determined the most structural and optical characteristics of catalysts and the suitable conditions of photocatalytic reaction. Also, chemical and catalytic stability were investigated.

2. Experimental section

2.1. Materials and products

Two natural iron-oxides were obtained from iron-ore career situated at Tamra region in the north-West of Tunisia.

Anionic dye Congo red (CR) was obtained from Sigma Chemical, and it was used without further purification, it is a secondary diazo dye. Working solutions were prepared by further dilution of the stock solution. In order to adjust the acidity of the solutions, 0.10 mol·L^{-1} sodium hydroxide or hydrochloric acid solutions were used. Molecular structure of the dye is represented in Fig. 1.

Hydrogen peroxide H_2O_2 (35%, w/w) was of analytical grade.

Other chemicals, including NaOH and HCl were all obtained with high purities.

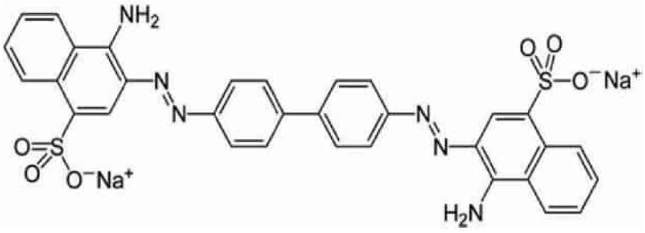

Fig. 1. Congo red structure.

2.2. Preparation and characterization of the catalysts

The crystal structure was characterized by X-ray diffraction (XRD) on the diffractometer (PANalytical X'Pert High Score plus diffractometer) with monochromatic radiation CuKα (λ= 1.5406 Å). The Fourier transform infrared (FTIR) spectra of the samples were recorded on a Perkin Elmer 783 dispersive spectrometer in the range of 4000–400 cm^{-1}. Specific surface area (BET), pore size (BJH), and pore volume (Vp) of the related catalysts were determined using the N_2 adsorption-desorption method with a gas adsorption analyser at 77 K using liquid nitrogen (Quantachrome model Nova 1000e surface and porosity analyzer), and the tested samples were degassed at 497 K for 2 h in a vacuum prior to analysis. The chemicals compositions of the samples were determined by X-ray fluorescence. All XRF measurements were performed with a commercial instrument (ARL 9900 of THERMOFISCER), using monochromatic radiation $K\alpha_1$ of cobalt (λ = 1.788996 Å). The optical properties were investigated using UV-vis diffuse reflectance Spectroscopy (DRS) using UV-visible spectrophotometer (Shimadzu UV-2700). Time-resolved photoluminescence (PL) was performed on a FLS980 Spectrometer by applying laser excitation at 400 nm.

2.3. Quartz glass reactor illuminated with UV lamp

The photo-reactor used is a Pyrex cylinder and its volume is 1 L. Irradiation was provided by a 125 W Philips HPK UV-lamp (UV-A,) placed in a plugging tube. A Pyrex cylindrical jacket located around the plugging tube allows an irradiation with wavelengths, λ = 350 nm.

2.4. Batch experimental procedures for adsorption studies

In this experiment, 0.1 g of iron oxide catalyst was placed into flask containing 50 mL of dye solution. The initial pH of Congo red solution was fixed at neutral pH. The mixture was maintained under stirring in the dark for 100 min for different dye concentration to evaluate the effect of initial dye concentration and to determine when the adsorption-desorption equilibrium was established. After that, the absorbent was separated from the dye solution by centrifugation for 20 min and filtered through a 0.45 μm filter. Then, the amount of dye which not adsorbed in the solid phase was determined using UV-vis spectrophotometer (Shimadzu Model Perkin Elmer) and the absorbance measurements were made at the maximum wavelength of CR at 498 nm.

The percentage adsorption (% Adsorption) was calculated by the following relationship:

$$\%Adsorption = 100 * \frac{(C_0 - C_e)}{C_0} \quad (1)$$

where C_0 and C_e are the initial concentration and equilibrium concentration of CR.

2.5. Batch experimental procedures for photooxidation studies

Every test is beginning with the addition of an appropriate catalyst masse to an aqueous solution of dye at desired value of pH. The preliminary path of each experiment consisted of the "dark" reaction as the lamp is kept "off". During this phase, dye adsorption is the solely physico chemical phenomenon taking place. Similar published works about heterogeneous catalysis reports the same methodology, in fact the adsorption phase precede the oxidation phase [25,26]. After that, when equilibrium adsorption-desorption is established, the desired amount of hydrogen peroxide was added and the lamp is turned "On". Hence, the catalyst is activated and the photooxidation reaction is initiated. This procedure keeps till very low levels of dye are achieved and complete dye mineralization is done. During reaction time, dye samples are withdrawn at different intervals time. Those samples are analyzed using several analytical techniques to determine the dye and the final products concentrations.

The degradation percentage (% degradation) of Congo red was calculated using the following equation:

$$\%Degradation = 100 * \frac{(A_0 - A_t)}{A_0} \tag{2}$$

Here, A_0 is the initial concentration and A_t is the equilibrium concentration at time t.

2.6. Analytical methods

During photooxidation process, dye concentration was determined by means of a Young Lin YL 9100 high-performance liquid chromatography (HPLC) instrument equipped with C 18 reverse phase column and UV-vis spectrophotometer detector. Mobile phase consisted of acetonitrile/water = 40/60 (v/v), flow rate 1 mL·min^{-1}, injection volume was 20 µL and detector wavelength 498 or 564 nm. Ion chromatography was recorded to confirm the mineralization by the quantification of NO_3^- and SO_4^{2-} ions. All analysis were conducted with a metrosop A Supp 4 anionic column at 40°C using a mobile phase composed of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ at 1 mL·min^{-1}. The Fe ions leaching from the catalyst were measured using a 1300 Perkin Elmer atomic absorption spectrophotometer.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Powder XRD spectroscopy

The mineralogical composition of both photocatalysts was examined using XRD analysis and their corresponding patterns are shown in Fig. 2. The sharp diffraction peaks indicate the crystalline nature of the studied photocatalyst. Also, it can be seen that the same diffraction peaks have appeared in the XRD spectra of two samples. The diffraction peaks at 21.2°, 34.96°, 36.8°, 41.4°, 50.5°, 53.2° and 59.3° are assigned to the presence of goethite FeOOH [28,29], those at 33.22°, 40.5° and 68.3° are related to the presence of Hematite Fe_2O_3 [30] and magnetite phase Fe_3O_4 is identified by these diffraction peaks 35.5° and 61.3° [31]. We notice the presence of other secondary phase peaks like quartz and kaolinite. This is due to the impurities phases presented in natural materials.

3.1.2. BET surface area analysis

The N_2 adsorption-desorption isotherms and their corresponding Barrett-Joyner-Halenda (BJH) pore size distribution curve were given in order to examine the surface area of the studied photocatalysts. As shown in Fig. 3, the adsorption-desorption isotherms of two samples are a type IV isotherm with a hysteresis loop according to UIPAC classification [32]. The specific surface area BET of MF and MF03 was measured to be 44.3 and 45.86 m^2/g respectively. Also, the most probable values of samples pore size are about 2 nm which means that both photocatalyst

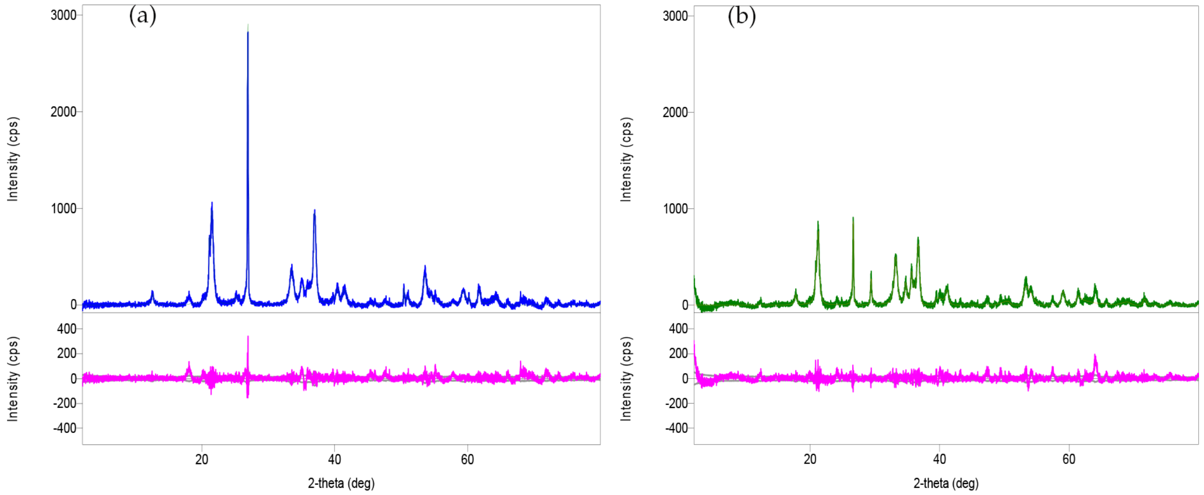

Fig. 2. Powder X-ray diffraction patterns of MF and MF03.

have micro porous structure. The efficient degradation is attributed to the higher porosity and high surface area of the photocatalyst.

3.1.3. UV-vis spectroscopy and photoluminescence studies

Fig. 4A shows the UV-vis diffuse reflectance spectra of both photocatalyst. It can be seen that both substrate exhibited absorption in the visible light region. However, MF sample exhibited two remarquables edges absorption over the entire visible light region at 600 nm and 760 nm. These results confirmed that the optical responses of both samples could be extended to the visible light region. Hence, this visible light energy could be utilized by iron oxides for realizing the photocatalytic activity. Tanwar et al. [26] report the same remark in their work, PANI/Fe° doped BiOCl can be easily activated by visible light (200–800 nm).

PL studies are useful to find the different optoelectronic nature of both iron oxides studied. The room temperature PL spectra of MF and MF03 are shown in Fig. 4B The spectra show emission band at 550 nm for both photocatalyst. It can be seen that PL emission intensity of the MF sample is lower than that of MF03. According to Li et al. [33] catalyst, with lower PL intensity, has less recombination of photo-induced electron-hole pairs. Hence, when the recombination rate decreases, more photo-generated charge carriers can participate in the photochemical transformation, resulting in an enhancement in photocatalytic activity.

3.1.4. XRF analysis

Chemical compositions of the studied photocatalyst are illustrated in Table 1. It can be seen that the Fe amounts of both samples were higher than 50%. MF03 contains the highest value of value of iron 64.12% and MF contains 50.8%. Fe, Ca and Si are the most abundant elements in the samples.

3.2. Adsorption study

The kinetics of adsorption of Congo red in the dark was studied on the photocatalyst MF for 100 min for different initial concentration on the dye. Results are represented in Fig. 5. It can be seen that the adsorption equilibrium reached within 60 min independently of the initial concen-

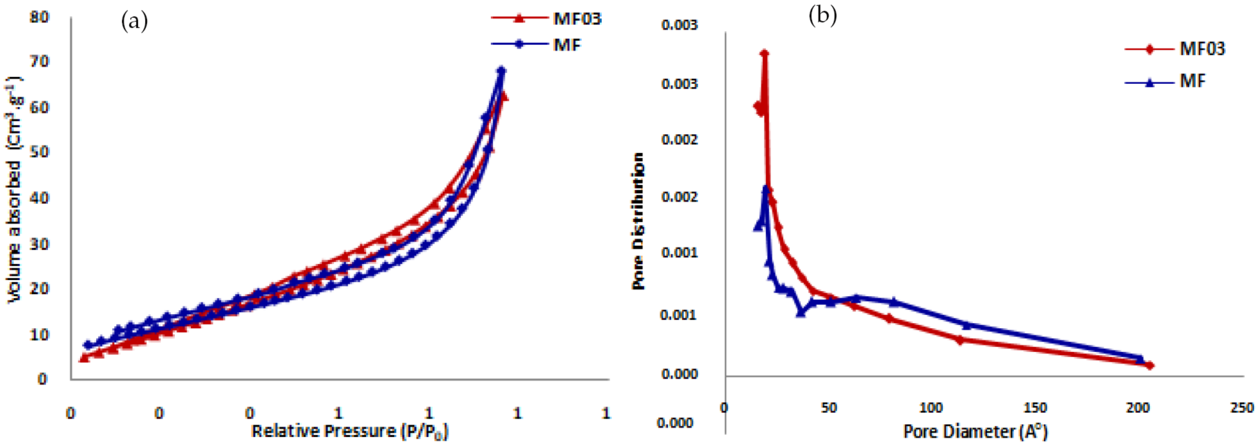

Fig. 3. (A) N_2-adsorption-desorption isotherm (BET) and (B) BJH pore size distribution of MF and MF03.

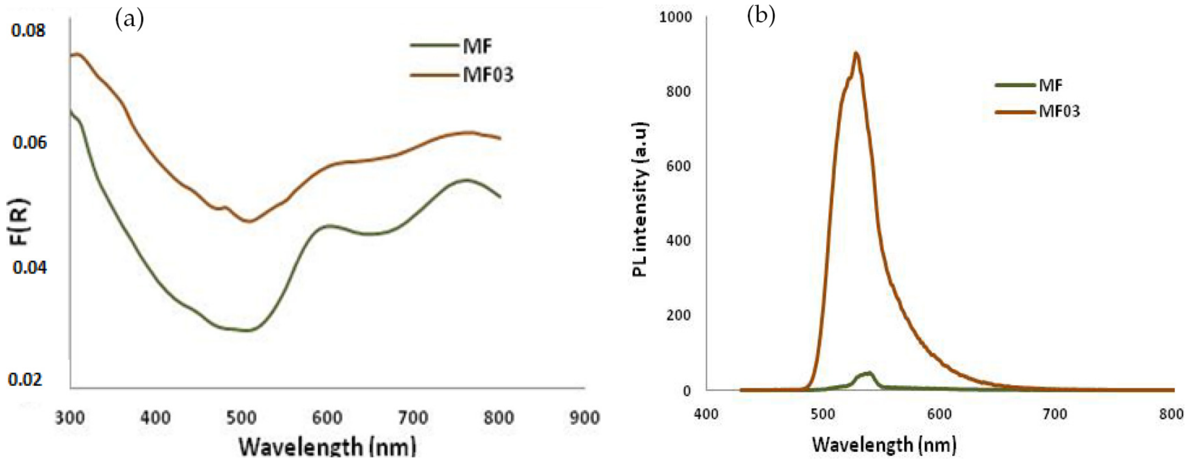

Fig. 4. (A) UV-vis spectra in reflectance diffuse and (B) Photoluminescence spectra excited at 400 nm of both photocatalysts: MF and MF03.

Table 1
Chemical composition and textural properties of photocatalysts

Sample	MF	MF03
Fe (%)	50.8	64.12
Si (%)	15.38	13.66
Ca (%)	4.87	6.29
Al (%)	5.03	3.9
Mg (%)	0.77	0.69
Cr (%)	0.02	0.02
SBET (m^2/g)	44.39	45.87
D (Å)	19.07	18.9
V_{ads} (cm^3/g)	0.11	0.10

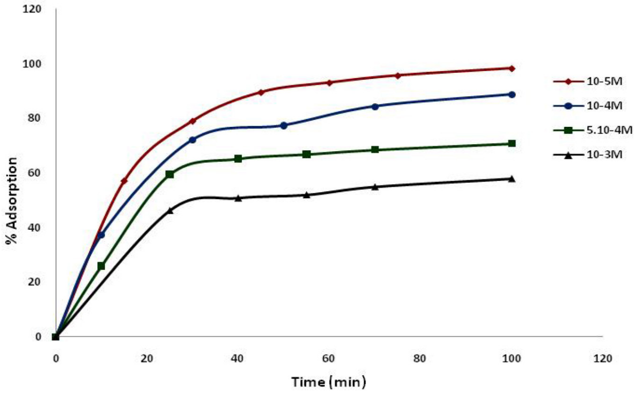

Fig. 5. The kinetics of the adsorption of Congo red on iron oxide catalyst MF at different concentration.

tration. Also, iron oxide presents a high adsorption capacity especially for low concentration. Hence, the adsorption percent can reach 96%, 88%, 70% and 58% in 100 min for 10^{-5} M, 10^{-4} M, $5{\cdot}10^{-4}$ M and 10^{-3} M respectively. According to these results, the concentration of 10^{-4} M can be retained for the photocatalytic experiments in this study.

3.3. Photocatalytic degradation

3.3.1. Adsorption and reaction of model pollutants

Prior to running the photo-Fenton reaction, Congo red adsorption into MF catalyst was determined. Hence, it is very important to know if the Congo red's color disappears as adsorption reaction or photooxidation reaction. So, establishing the adsorption-desorption, adding the oxidant and turning the lamp "On" is the way followed in all photo-Fenton experiments. Fig. 6 shows the change of CR liquid phase concentration with time. As shown, Congo red removal via adsorption onto MF sample was found to be important after 60 min (removal efficiencies = 88 %) compared to removal via photo-Fenton process.

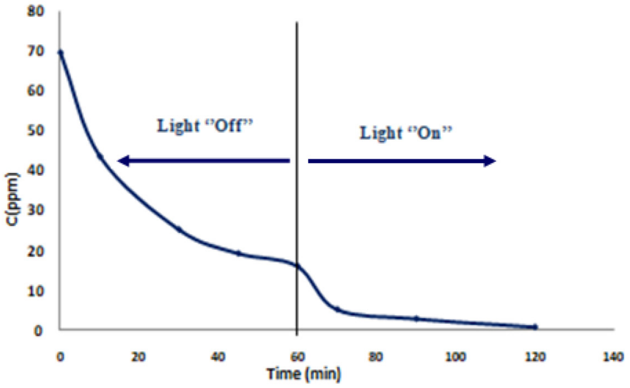

Fig. 6. Change of Congo red liquid phase concentration with time: Initial concentration = 10^{-4} M.

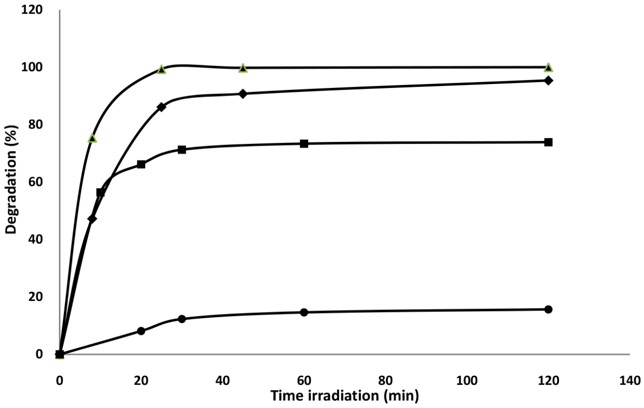

Fig. 7. Photodegradation of Congo red under different system: ▲UV/H_2O_2/MF; ♦ UV/H_2O_2/MF03; ■ UV/H_2O_2; ● UV alone.

3.3.2 Congo red Photo-Fenton degradation

Photocatalytic degradation of CR diazo dye investigated in this study is shown in Fig. 7. As can be shown, Congo red was highly resistant to photolysis with UV light irradiation alone. On the other hand, in the case of UV light irradiation combined with H_2O_2, CR degradation efficiency was 70% because UV light catalyzed H_2O_2 to generate the HO. radical. In the system with UV/H_2O_2/MF03, the degradation efficiency achieved 90% within 45 min but it still not an ideal photo-Fenton catalyst. When MF was used, the degradation (%) reached 99.76% for the first 45 min, and a greater enhancement in photo-Fenton degradation was achieved, resulting in an almost complete removal of CR within 1 h. This suggested that MF exhibits a better catalytic activity than MF03. This is in reasonable agreement with the results obtained from BET analysis indicating that MF presents the higher surface area which could increase the number of adsorbed molecules of CR.

Photocatalytic activities of the natural iron oxide are estimated by observing the UV-vis spectra changes of Congo red solutions during the photo-Fenton reaction as function of time using 0.1 g MF as photocatalyst. Results are shown in Fig. 8. As can be seen, the absorption spectrum of CR is characterized by a strong absorption peak at 497 nm. As the reaction proceeded, we noticed a reduction in the optical absorption band and a disappearance after 60 min. The continuously decrease of the band at 497 nm with the reaction

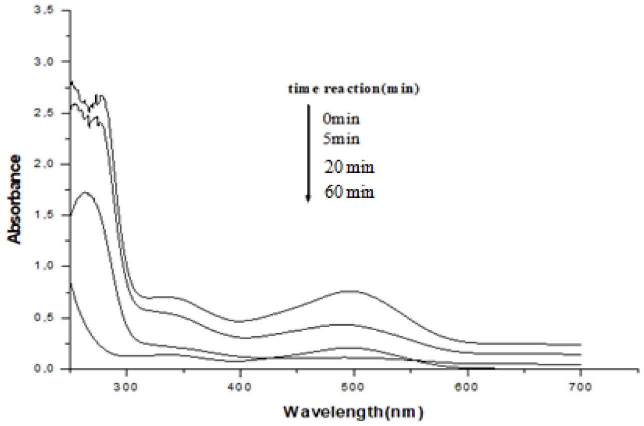

Fig. 8. Absorption spectra of CR in the presence of MF photocatalyst under UV light irradiations.

Table 2
Characteristics of the real textile industries effluent before and after photo-Fenton treatment

Parameters	Value	Treated wastewater
pH	10	8
TOC (mg/L)	10	0.9
BOD5 (mg/L)	600	70
COD (mg/L)	1400	50
Colour	3500	140
Suspended solids (mg/L)	200	traces
Total hardness (mg/L)	100	traces
Oil and grease (mg/L)	10	traces
TDS (mg/L)	3500	2000
Chloride (mg/L)	1700	400

time indicated the total discoloration and the destruction of azo-band system.

Additionally, dye mineralization was monitored using ion chromatography analysis by the quantification of final NO_3^- and SO_4^{2-} ions in the solution. Then results indicate that after 1 h of photo-Fenton treatment, the MF catalyst allow the total mineralization of initial N heteroatom to SO_4^{2-}, about the initial N groupment, it can be concluded that MF give a major loss of N as NH^{4+} or volatile N-compounds.

3.4. Photodegradation of real textile industries effluent

According to results obtained with Congo red, we choose to apply photo-Fenton oxidation with the photocatalyst MF in the treatment of a real textile industries effluent. Hence, a sample was sampled in the output of a textile industry SITEX located in the eastern of Tunisia. Table 2 illustrates the most characteristic of the effluent before and after 3 h treatment. It can be seen that the photocatalytic activity of this catalyst was efficient in the degradation of the effluent. But, the degradation rate in this case was slower than in the case of CR. This is due to the complex composition of effluent; it is a mixture of organic compounds. The TOC and COD measurements after photo-Fenton treatment clearly indicate a highest activity of natural catalyst. The percentage mineralization was almost total after 3 h.

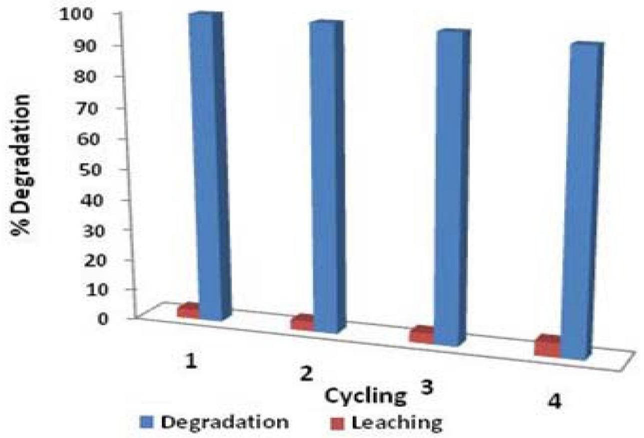

Fig. 9. Cyclic photodegradation of CR by MF (Test conditions: 10^{-4} M dye concentration, 10 mM H_2O_2, 25°C and 0.1 g of catalyst).

Table 3
Stability of catalyst MF at different cycles

Cycling	Removal (%)	Iron leaching (mg/L)
1	99.98	4.16
2	98.05	5.18
3	96.35	5.67
4	95.03	6.75

3.5. Catalyst reusability

Via thinking about environmental and economic benefits, catalysts stability has been evaluated in four consecutive CR degradation reactions. Each test was carried out under identical conditions, after each experiment, the solution was filtered, washed and collected catalyst was dried to be used again to degrade CR. It can be seen in Fig. 9 that the photocatalyst MF reused in multiple runs and their activity was kept during the reaction. Also, concentration of iron in the solution was measured by SAA in this study and results indicate that the iron ion leaching from iron oxide is negligible (Table 3). These results clearly reveal that natural iron oxide can serve as a good reusable photocatalyst.

In order to compare this study with others and specify its importance in research, Table 4 presents a comparative study between results in terms of the degradation efficiency, considering different catalyst based on iron-oxide material and different pollutant.

Based on these results, we can conclude that the used catalyst in this study present a good catalytic activity compared with others from different origins.

4. Conclusion

UV light irradiated photo-Fenton degradation of Congo red diazo dye using locally iron oxide was investigated in

Table 4
Comparison of catalytic efficiencies and time for different catalysts

Catalyst	Pollutant	Degradation (%)	References
Natural vanadium-titanium magnetite	Acid orange II	98% (t = 4 h)	[34]
Mixed oxide of iron and silica	Methyl red	90% (t = 3 h)	[35]
Titanomagnetite	Tetrabromobis-phenol	100% (t = 4 h)	[36]
Natural iron oxide	Congo Red	100% (t = 60 min)	This work
Nanostructured magnetite (MGN1)	Paracetamol	50% (t = 5 h)	[37]
Maghenite nanoparticles (NP)	Methylene blue	82% (t = 5 h)	[38]

this work. A particular care has been given to structural and optical properties of studied materials.

The results obtained indicate that natural Tunisian iron oxide is an efficient catalyst for the degradation of diazo dye and real textile effluent under UV light irradiations. Degradation of CR was mostly carried through heterogeneous Photo-Fenton reaction and homogeneous reaction was negligible according to result obtained by leaching tests.

Congo red can be completely degraded within 60 min under UV light irradiations with 0.1 g of catalyst MF and total mineralization was reached 100% by quantification of SO_4^{2-} ions. Also, reutilisability experiments showed that iron oxide was stable and can be used for several tests without loss in catalytic activity or chemical structure.

Finally, the iron oxide/H_2O_2/UV system is a promising process for dye mineralization and or the treatment of real effluent textile industries.

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