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Cationic Dye Degradation and Real Textile Wastewater Treatment by Heterogeneous Photo-Fenton, Using a Novel Natural Catalyst

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Abstract: A photo-Fenton process using a local iron oxide as a natural catalyst was compared to Fenton and UV/H₂O₂ advanced oxidation processes for degrading crystal violet (CV) dye in aqueous solutions. The catalyst was characterized by transmission electron microscopy (TEM), energy dispersive X-ray microanalysis (EDX), Fourier transform infrared spectroscopy (FT-IR), Raman spectrum, X-ray diffraction (XRD), UV-vis spectroscopy, and Brunauer–Emmett–Teller (BET) analysis. The optical properties proved that the catalyst represents a good candidate for photocatalytic activity. The impact of different parameters (catalyst dose, initial CV concentration, initial H₂O₂ concentration, pH) on the photo-Fenton efficiency was evaluated. A photo-Fenton process operated under UVC light irradiation, at spontaneous pH, with 1.0 g/L of catalyst and 30 mg/L of H₂O₂ was the most effective process, resulting in 98% CV dye removal within 3 h. LC-MS and ion-chromatography techniques were used to identify demethylated organic intermediates during the process. Furthermore, a regeneration study of the catalyst showed its stability and reusability (after three treatment cycles, CV dye degradation decreased from 94% to 83%). Finally, the photo-Fenton process was tested in the treatment of real textile wastewater, and the effluent was found to be in compliance with standards for industrial wastewater disposal into sewerage.

Keywords: advanced oxidation processes; crystal violet dye; heterogeneous catalyst; iron oxide; regeneration; real wastewater

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1. Introduction

Dyes are organic compounds often utilized in the paper, plastic, pigment, cosmetic, and textile industries [1,2]. Textile factories produce wastewater characterized by a very low biodegradability, high amounts of surfactants, high chemical oxygen demand (COD), toxicity, highly fluctuating temperature and pH, and a strong color [3,4]. These textile effluents represent a serious problem for the environment, and even their degradation products may be toxic, thus threatening public health and aquatic organisms [5].

Several methods have been tested to remove dyes from water, including membrane separation [6], conventional coagulation/flocculation [7] and adsorption [8]. Unfortunately, these methods can only transfer pollutants from liquid to solid phase. Moreover, several dyes are not biodegradable, making a biological process alone not a suitable solution for textile wastewater treatment. Advanced oxidation processes (AOPs) are a possible solution for degrading bio-refractory pollutants. These processes promote the formation of highly reactive and non-selective oxidants species, such as hydroxyl radicals (•OH) that can degrade and mineralize recalcitrant compounds and eventually obtain non-toxic inorganic

molecules, such as CO_2 and H_2O [9]. Among them, Fenton reaction (iron salts + hydrogen peroxide) based processes are particularly effective for industrial wastewater treatment, to improve biodegradability before the biological process [10]. Unfortunately, Fenton-based processes are effective at acidic pH, because iron starts to precipitate at $\text{pH} > 3$, thus resulting in an environmental problem (sludge production) and increased treatment costs, due to wastewater acidification and the subsequent pH neutralization before the biological process [11]. In order to overcome these drawbacks, different approaches have been investigated in recent years. One approach includes chelating agent addition to promote the formation of complexes with metal species, making (photo) Fenton process effective, even at neutral pH [12,13]. However, while effective in tertiary treatment of urban wastewater, the addition of chelating agents can be quite problematic when applied to remove organic pollutants in high concentrations, such as in industrial wastewater treatment [14]. Another approach has been established with the utilization of solid phase (photo) catalysts (heterogeneous photo-Fenton). In the photocatalytic degradation of dyes, many iron oxides have been investigated in previous studies, regarding their impressive photocatalytic activity, structural stability, and narrow band gap, such as magnetite, goethite, and hematite [15]. However, most of the works available in the scientific literature only investigated the effect of the process on dye aqueous solutions [16], not taking into account the interference of other substances (such as dissolved organic matter), typically occurring in real wastewater. Accordingly, investigations on real wastewater are highly advisable, to evaluate the effect of the processes under realistic conditions and to speed up their possible applications at industrial scale. Moreover, to make the process sustainable and economically affordable, potentially reusable, stable, and cheap catalysts are desirable and worthy of investigation.

In this study, a heterogeneous photo-Fenton process using a new natural iron oxide as catalyst was evaluated for the degradation of crystal violet (CV) dye and compared to Fenton (iron oxide + H_2O_2) and UV/ H_2O_2 processes for the first time. CV was used as model dye because it is one of the most widespread and recalcitrant dye molecules, which has toxic effects in the environment [17] and it is a potent carcinogen and clastogene that boosts the growth of tumors in some species of fish [18]. Control tests with photolysis (UV) and oxidation (H_2O_2) were also carried out. The catalyst was characterized by transmission electron microscopy (TEM), energy dispersive X-ray microanalysis (EDX), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Raman spectroscopy, UV-vis diffuse reflectance spectroscopy (DRS), and Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) analyses. AOPs can lead to the formation of oxidation intermediates that can be even more toxic than the parent substances [19], accordingly CV intermediates were also analyzed by LC/MS and ion-chromatography. Catalyst reusability tests were also carried out. Finally, the photo-Fenton process with this new catalyst was also investigated in the treatment of real textile wastewater.

2. Results and Discussion

2.1. Catalyst Characterization

2.1.1. XRD, Raman, and FT-IR Analysis

XRD characterization of the catalyst (Figure 1a) indicates peaks relevant to hematite (Fe_2O_3) at $2\theta \sim 34$, ~ 40.2 and ~ 64 [20], magnetite (Fe_3O_4) at $2\theta \sim 21.5$, ~ 30 , ~ 37 and ~ 61.5 [21], goethite (FeOOH) at $2\theta \sim 15.1$, ~ 24.5 , ~ 35 , ~ 35.70 , ~ 41.4 , ~ 50.2 , ~ 53.4 and ~ 59.2 [22], Kaolinite ($2\theta \sim 9$) and quartz ($2\theta \sim 26$).

IR spectrum of the catalyst (Figure 1b) indicates two absorption bands at 480 and 560 cm^{-1} , which represent the vibration bands of Si–O and O–Fe–O functional groups, respectively [23]. Both bands at 890 and 784 cm^{-1} are related to the vibrations in and out of the plane of O–H bending bands in goethite phase [24,25]. Bands at 1041 and 1642 cm^{-1} are assigned to the asymmetric stretching vibration of Fe–O–Si and O–H, respectively. The band at 1451 cm^{-1} is attributed to asymmetric stretching vibration of C=O [25]. Finally, the band at 3388 cm^{-1} is related to O–H stretching vibration in hydroxyl groups [26].

Figure 1. XRD pattern (a), IR spectrum (b), and Raman spectrum (c) of the catalyst.

Raman spectrum of the catalyst (Figure 1c) in the wavelength range of 150–1200 cm^{-1} is characterized by many peaks. Bands at 180 cm^{-1} and 288 cm^{-1} are attributed to hematite phase in the natural iron oxide [27]. Magnetite phase is mostly identified by the existence of a band at 602 cm^{-1} [28]. Bands at 417 and 495 cm^{-1} can be assigned to goethite phase, as reported in previous studies [29,30]. The two bands at 956 and 1013 cm^{-1} are associated with Siderite phase [27].

2.1.2. TEM–EDX and DRS Analyses

A TEM micrograph of the catalyst (Figure 2a,b) shows rod shaped structures with various thicknesses and lengths, according to previous works [31]. A good dispersion of iron oxide rods is expected to enhance the photocatalytic activity. EDX analysis (Figure 2c) indicates the existence of several elements such as Fe (wt% = 63.6), Si (wt% = 30.2), Al (wt% = 3.2), As (wt% = 1.7), and Mg (wt% = 1.3), confirming the results of the XRD and Raman analyses. The significant amount of Fe proves that this material can be successfully used as a catalyst in Fenton and photo-Fenton processes.

Figure 2. TEM micrographs at different scales: (a) 100 nm and (b) 200 nm; (c) EDX spectrum; (d) DRS of the catalyst.

DRS spectrum (Figure 2d) reveal three absorption peaks at $\lambda = 280$ nm, 610 nm and 750 nm, respectively, suggesting the good optical response of the catalyst under UV and visible light regions for photocatalytic activity.

2.1.3. BET and BJH Analyses

According to IUPAC classification, the BET adsorption isotherm of the catalyst (Figure 3) displays a curve of type IV with a hysteresis loop [32].

Figure 3. N₂ Adsorption/desorption isotherm of natural iron oxide.

A BJH method using desorption isotherms allowed quantifying the iron oxide total pore volume as 0.1 cm³/g (Figure 3, Table 1). Specific surface area of the catalyst was estimated as 45.86 m²g^{−1} using BET method (Table 1). The mesoporous surface area and volume values as obtained by BJH method are also displayed in Table 1.

Table 1. Textural properties of the catalyst.

S_{BET} (m ² /g)	$S_{\text{BJH/mesp}}$ (m ² /g)	$V_{\text{BJH/mesp}}$ (cm ³ /g)	V_{ads} (cm ³ /g)	D (Å)
45.86	44.17	0.092	0.1	20

S_{BET} : BET surface area; $S_{\text{BJH/mesp}}$: mesopore surface area; $V_{\text{BJH/mesp}}$: mesopore volume; V_{ads} : volume of N₂ adsorbed at $P/P_0 = 0.98$; D: average pore diameter.

Notably, owing to a larger surface area, more catalytically active sites are available and can improve the photocatalytic activity [33].

The pore size distribution (inset in Figure 3) supports the mesoporous framework of the catalyst, according to IUPAC, with an average pore size of 2 nm (peak at pore diameter = 2 nm) [34].

2.2. Degradation of CV Dye in Aqueous Solution by AOPs

2.2.1. Dark Adsorption Test

Dark tests with the catalyst were carried to evaluate the adsorption process contribution to CV dye removal, as well as the time needed to achieve adsorption–desorption equilibrium. The maximum adsorption of CV dye by the catalyst was as high as 70% and

the adsorption–desorption equilibrium was reached within an hour (Figure 4), which is consistent with a relevant previous adsorption study [35].

Figure 4. Kinetic of CV dye adsorption onto natural iron oxide ((CV) = 10 mgL^{-1} , $m_{\text{cat}} = 0.1 \text{ g}$, $T = 25^\circ \text{C}$).

2.2.2. Photo-Fenton Experiments

The photo-Fenton process was compared to Fenton and H_2O_2 /UV processes. Control tests by photolysis and H_2O_2 , as standalone processes, were also carried out under fixed initial conditions (1.0 g of catalyst/L, 30 mg H_2O_2 /L, room temperature, neutral pH (6.7)). The results clearly show that photo-Fenton was the most effective among all the tested processes, achieving 94% removal efficiency after 180 min (Figure 5). The contributions to CV degradation by photolysis and direct oxidation with H_2O_2 were quite poor (6% and 18% after 180 min, respectively). The UV/ H_2O_2 advanced oxidation process was more efficient than UV and H_2O_2 separately, but still poorly effective (only 39% after 180 min treatment) compared to the Fenton and photo-Fenton processes, consistent with a previous work [36]. The final efficiency of the Fenton process (85%) was comparable with the photo-Fenton, but the degradation rate was slower, making photo-Fenton potentially more attractive, due to the reduced volume necessary to achieve a high degradation rate.

2.2.3. CV Dye Degradation by Photo-Fenton Process: Effect of Different Parameters

Effect of the Initial Pollutant Concentration

The removal efficiency of CV by photo-Fenton decreased from 99% to 80% by increasing the initial dye concentration from 5 to 20 mg/L (Figure 6a). These results can be explained by the fact that higher concentrations of the pollutant increased the pollutant/radicals ratio, as well as decreasing the penetration of photons, due to the darker color of the aqueous solution [37].

Effect of Catalyst Dose

The influence of the catalyst mass on dye degradation via photo-Fenton process was also investigated by varying the catalyst dose from 0.5 to 2.0 g/L and keeping constant the other operating parameters. The CV removal efficiency increased as the catalyst dose was augmented from 0.5 g/L to 1.0 g/L, and decreased when the catalyst dose was further increased up to 2.0 g/L (Figure 6b). This behavior is typical for a heterogeneous photocatalytic process. The efficiency improved as the catalyst loading was increased up to achieving a maximum pollutant removal; then started to decrease for further additions

of the catalyst, due to the increased opacity of the aqueous solution, which prevents the penetration of photons, thus reducing the radical yield [38]. Accordingly, the optimum catalyst dose in this study was found to be 1.0 g/L.

Figure 5. CV dye removal under different tested processes.

Figure 6. Cont.

Figure 6. Effect of pollutant concentration (a), catalyst dose (b), pH of CV solution (c), and oxidant concentration (d) on the CV dye degradation by photo-Fenton.

Effect of pH

It is well-known that in homogenous processes, pH can drastically affect the (photo) Fenton efficiency, with $pH < 3$ being the optimum condition. However, the main expected advantage in using iron oxide as a catalyst is related to the possibility of effectively operate the process under neutral pH conditions [39]. Due to the Fe(II)/Fe(III) species immobilized on the surface of the solid, an efficient redox system with H_2O_2 in a wider pH range is expected. Three different pH conditions were investigated, and the photo-Fenton process was found to be minimally affected by pH, with 100%, 94%, and 91% removals of CV observed at pH 4, 7 and 10, respectively (Figure 6c).

Effect of H_2O_2 Concentration

In photo-Fenton process, the catalyst dose, H_2O_2 concentration and their ratio are among the most relevant parameters, because they affect the active radical concentration yield. To evaluate the influence of hydrogen peroxide on the CV dye degradation, its initial concentration was varied from 5 mg/L to 100 mg/L. When the H_2O_2 concentration was

increased from 5 mg/L to 30 mg/L, the removal efficiency drastically increased from 34% to 86% (Figure 6d). This result can be explained by the higher radical production rate, due to the increased oxidant dose. However, further increases in H_2O_2 concentration (from 30 mg/L to 100 mg/L) resulted in a decreased removal efficiency (from 86% to 78%). This, only apparently, inconsistent result can be actually explained by the $\cdot\text{OH}$ radical scavenging activity due to hydrogen peroxide excess (Equations (1) and (2)) [40]:

Goethite, hematite and magnetite are among the common forms of iron oxide that can catalyze H_2O_2 to generate radicals and degrade organic pollutants [41]. In particular, some authors observed a similar decomposition of H_2O_2 catalyzed by goethite and hematite when normalized to the surface area [42,43]. Several mechanisms have been proposed to explain the degradation kinetics of pollutants through iron oxide catalyzed reactions in the heterogeneous Fenton process. According to the main one, $\cdot\text{OH}$ is an intermediate primarily responsible for the degradation of the target organic pollutant [44]. Due to the low concentration of dissolved iron, Lin and Gurol [45] proposed a mechanism for a goethite-catalyzed Fenton-like reaction, where diffusion and adsorption of H_2O_2 to the oxide surface takes place before the decomposition of H_2O_2 on the surface of goethite. An enzymatic-like activity similar to peroxidases has also been proposed as a possible mechanism for the degradation of pollutants by magnetite catalyzed Fenton process, through the intermediates generated between H_2O_2 and magnetite [46,47].

In conclusion, 30 mg/L was the optimum H_2O_2 concentration to degrade CV dye by photo-Fenton process under the investigated conditions.

The residual concentration of H_2O_2 during the process was also monitored and an almost total consumption was observed after a three hour treatment (Figure 7).

Figure 7. Degradation of CV dye and H_2O_2 consumption during the photo-Fenton process under optimum conditions ((CV) = 10 mg/L, (H_2O_2) = 30 mg/L catalyst concentration 1.0 g/L).

If we compare the results achieved under optimum conditions with those available in the scientific literature for other iron based catalysts, we can see that it is very competitive in terms of process efficiency (Table 2).

Table 2. Comparison of natural iron oxide with different photocatalysts for CV dye degradation by photo-Fenton process.

Catalyst	Operating Conditions	Degradation Percentage	Reference
Fe-Montmorillonite	Dosage: 0.15 g/L; (H ₂ O ₂) = 50 mM; (CV) = 0.06 mM, visible light irradiation	90%	[48]
K ₂ Fe ₄ O ₇	Dosage: 0.03g/L; (H ₂ O ₂) = 5 mM; (CV) = 20 mg/L, visible light irradiation	92%	[5]
Fe ₃ O ₄ -polydopamine-bentonite composite	Dosage: 0.03g/L; (H ₂ O ₂) = 1 mM; (CV) = 20 mg/L; UV light irradiation	93%	[49]
Natural iron oxide	Dosage: 1g /L; (H ₂ O ₂) = 30 mg/L; (CV) = 10 mg/L, UVC light irradiation	98%	This work

2.3. Kinetic Study and Oxidation Intermediates Characterization

2.3.1. Kinetic Study

The photocatalytic degradation of organic pollutants is typically well-described using a pseudo-first-order (PFO) model, used herein to evaluate the kinetic degradation of CV dye by photo-Fenton reaction through the following equation:

$$\ln\left(\frac{C_0}{C_t}\right) = k \cdot t \quad (3)$$

t (min) is the irradiation time, C_0 and C_t are the initial and time t concentrations of the pollutant (CV) (mg/L), respectively, k (min^{−1}) is the pseudo-first order rate constant for the pollutant degradation, which is calculated by plotting $\ln(C_0/C_t)$ Vs the irradiation time t .

The formation of oxidation intermediates may result in the misinterpretation of the experimental data when the degradation of the target pollutant is monitored through UV absorbance measurements, which is not a target analysis. As a matter of fact, the intermediate organic compounds are in turn degraded by the photocatalytic process to a rate which depends on their refractoriness to the treatment process [50]. This behavior can be identified by plotting all the data of the experimental test according to the same kinetic (in this case PFO) and identifying the points of discontinuity (n) and the corresponding PFO kinetics ($n + 1$) [50]. In this case, the points of discontinuity are two, and therefore it is possible to extrapolate three PFO kinetics with different slopes and plot them accordingly (Figure 8).

Figure 8. Plot of the pseudo-first-order model of CV dye photocatalytic degradation.

The corresponding kinetic parameters are given in Table 3. The higher slope of the first kinetic (Y_1) in the early 30 min can mainly be ascribed to the faster initial degradation of the parent compound (CV). The degradation of more refractory oxidation intermediates may explain the drastically decreased slope of the second kinetic (Y_2). Finally, the faster kinetic observed in the third step (Y_3) can be ascribed to the degradation of less refractory, and subsequently formed, oxidation intermediates.

Table 3. The PFO Kinetic parameters of CV degradation during the heterogeneous photo-Fenton process (conditions: spontaneous pH, CV = 10 mg/L, H_2O_2 = 30 mg/L, catalyst concentration 1.0 g/L).

PFO Kinetic ($Y_i = a_i \cdot x + b_i$)	$6.8 \times 10^{-2} \cdot x + 0.1$	$4.7 \times 10^{-4} \cdot x + 2.107$	$8.0 \times 10^{-3} \cdot x + 1.369$
R_i^2	0.982	0.992	0.995
k_i (min^{-1})	2.726×10^{-3}	5.206×10^{-6}	0.0076
a_i	0.1498	2.10721	1.36934
b_i	0.06818	4.69515×10^{-4}	0.00836

2.3.2. Characterization of Oxidation Intermediates

The CV dye demethylated intermediates formed during the photo-Fenton process were detected using LC-MS (Table 4). In addition, an ion chromatography technique was used to detect anionic and cationic by-products of the dye, which were acetate (CH_3COO^-), formate (HCOO^-), Cl^- , and NH_4^+ . These results are in agreement with previous reports [51,52] and prove the effectiveness of the photo-Fenton process to turn CV dye into less- or non-toxic products [51].

Table 4. Molecular structure, chemical names, and m/z values of demethylated intermediates of CV dye detected by LC-MS.

Molecular Structure	Chemical Name	m/z Value
<i>N,N,N',N'',N''',N''</i> -hexamethyl pararosaniline (Crystal violet)	372.14
<i>N,N</i> -dimethyl- <i>N',N'</i> -dimethyl- <i>N''</i> -methyl pararosaniline	358.18
<i>N,N</i> -dimethyl- <i>N'</i> -methyl- <i>N''</i> -methyl pararosaniline	344.16
<i>N,N</i> -dimethyl- <i>N',N'</i> -dimethyl pararosaniline	344.10

Table 4. Cont.

Molecular Structure	Chemical Name	m/z Value
<i>N</i> -methyl- <i>N'</i> -methyl- <i>N''</i> -methylpararosaniline	330.15
<i>N,N</i> -dimethyl- <i>N'</i> -methylpararosaniline	330.15
<i>N</i> -methyl- <i>N'</i> -methylpararosaniline	316.25
<i>N,N</i> -dimethylpararosaniline	316.13
<i>N</i> -methylpararosaniline	302.10
Pararosaniline	288.07
<i>N,N</i> -dimethyl aniline	121.15
<i>N</i> -methylaniline	107.06

According to the LC/MS and ion chromatography analyses, a mechanism can be proposed for the CV dye degradation, and this involves two different major pathways: (1) *N*-demethylation, and (2) cleavage of the chromophore bond structure [52,53]. This is due to the existence of two possible sites in the CV dye molecule for radical attack. During the *N*-demethylation route, the mono-, di- and tetra-methyl groups in the CV

molecules were attacked by $\bullet\text{OH}$ radicals, leading to the production of the following intermediates: *N,N*-dimethyl-*N'**N'*-dimethyl-*N''*-methyl pararosaniline, *N,N*-dimethyl-*N'*-methyl-*N''*-methyl pararosaniline, *N,N*-dimethyl-*N'*,*N'*-dimethyl pararosaniline, *N*-methyl-*N'*-methyl-*N''*-methyl pararosaniline, *N,N*-dimethyl-*N'*-methyl pararosaniline, *N*-methyl-*N'*-methyl pararosaniline, *N,N*-dimethyl pararosaniline and *N*-methyl pararosaniline. Then, the further degradation of the pararosaniline compound can lead to shorter chain hydrocarbons and less toxic ions. On the other hand, the cleavage of the CV chromophore ring structure route was marked by the appearance of aliphatic oxidation products, which were *N,N*-dimethyl aniline and *N*-methylaniline compounds. These results are in agreement with earlier findings reported in the literature [51,53,54].

2.4. Catalyst Regeneration and Stability

To evaluate the stability of the catalyst, the natural iron oxide employed in the previous tests was recovered and regenerated to check its stability and reusability. The photocatalytic activity of this catalyst was evaluated in three subsequent tests after a regeneration step and the addition of a fresh CV dye solution, under the same operating conditions. No significant reduction in the efficiency of CV dye adsorption on the catalyst after three regeneration cycles was observed (Figures 9a and 10). The catalyst maintained its adsorptive capacity (70%) and the CV dye degradation by photo-Fenton decreased from 94% to 83% (Figure 9a). Possibly, the reduced efficiency was due to the regeneration method, which did not allow a sufficiently efficient desorption process, making part of the adsorptions sites no longer available for the subsequent photocatalytic treatment tests. Therefore, to improve the regeneration process, either more intensive conditions (e.g., higher temperature) or different methods (e.g., photocatalyst washing with proper chemical desorption solutions) should be used. Furthermore, the morphology of the catalyst after three cycles (Figure 9b) was almost unchanged compared to the initial condition (Figure 2a,b). These results prove that the catalyst is stable and reusable for CV dye degradation.

Figure 9. (a) Removal efficiency of CV dye by natural iron oxide with different cycles; (b) TEM image after three successive cycles.

2.5. Real Textile Wastewater Treatment

Real textile wastewater was provided by a textile company in Tunisia, directly after the textile dyeing process and without any kind of treatment. The physico-chemical characteristics of the raw wastewater sample are provided in the Table 5. The investigated wastewater was a mixture of many dyes, such as Novacron Blue 4R (NB4R) and Bezaktiv Red S-Matrix (BRSM) and had a dark green color and maximum absorbance peak at 589 nm

(Figure 11). Textile wastewater treatment by photo-Fenton was investigated under different conditions, by increasing the catalyst dose from 1 g/L to 10 g/L and the H_2O_2 concentration from 30 mg/L to 1 g/L. Thus, the best option was found to be using 10 g/L of catalyst dose and 1.0 g/L of H_2O_2 at natural pH. As a matter of fact, this condition resulted in decreasing the intensity of the characteristic absorption peak of the raw effluent at 589 nm (Figure 11), drastically reducing COD, and making the effluent in compliance with standards for industrial wastewater disposal into sewerage (such as the Italian ones) (Table 5).

Figure 10. Photograph of (a) fresh catalyst, (b) catalyst after adsorption, (c) catalyst after three regeneration cycles.

Table 5. Main characteristics of the textile effluent before and after the photo-Fenton process, and comparison with Italian standards for industrial wastewater disposal into sewerage (D.Lgs 152/2006).

Quality Indicator	Raw Effluent	Treated Effluent	Italian Standards for Disposal of Industrial Wastewater into Sewerage
COD (mg/L)	803	290	500
Turbidity (NTU)	57	25	-
pH	9.18	8.31	5.5–9.5
BOD ₅ (mg/L)	352	149	250
Conductivity (μ S/cm)	15.05	13.51	-
TSS (mg/L)	130	Traces	200

Figure 11. UV-Visible spectra of the real effluent at spontaneous pH before and after treatment.

3. Methods and Materials

3.1. Reagents and Chemicals

CV ($C_{25}H_{30}N_3Cl$, M.W. = $407.98 \text{ g mol}^{-1}$) is a cationic dye (Figure 12a). It is widely used in paint, textile, and biotechnology industry. Its maximum absorption wavelength was experimentally found to be 583 nm (Figure 12b).

Figure 12. (a) Chemical structure and (b) UV visible spectra of CV dye.

The iron oxide used in this study was a natural material collected from iron-ore deposit located in the Nefza region (North-west Tunisia). The sample was dried and crushed to a small particle size. Chloride salt of CV, hydrogen peroxide (30% *w/v*) and titanium (IV) oxysulfate were purchased from Sigma-Aldrich (Germany) and used without any further purification. All the solutions were prepared in Milli-Q water. Reagent-grade ammonium acetate, nitric acid, sodium hydroxide, and HPLC-grade methanol were purchased from Merck. The pH was adjusted with the addition of proper volumes of 0.1 M HCl or 0.1M NaOH solutions.

3.2. Characterization of Catalyst

Different techniques were used to characterize the catalyst. Powder X-ray diffraction was performed using a PANalytical X'Pert HighScore Plus diffractometer, with monochromatic Cu-K radiation source ($\lambda = 1.5418 \text{ \AA}$) operated at 40 kV and 40 mA. The surface functional groups of the catalyst were investigated by FT-IR technique. The sample was grounded and mixed with KBr to make a pellet that was analyzed at a wavelength range of $480\text{--}4000 \text{ cm}^{-1}$ using a Perkin Elmer infrared spectrophotometer. Raman analysis was performed using a Raman spectrometer (Renishaw brand—inVia Raman) at room temperature, with an excitation laser line set at 632.8 nm from a He-Ne laser. TEM analysis was performed on a Philips FEI-Tecna 10 electron microscope operated at 200 kV. Quantitative analysis of the elemental composition was identified by EDX. Optical properties were tested by DRS, using a UV-visible spectrophotometer (Shimadzu UV-2700). Isotherm of nitrogen adsorption–desorption of material was measured using a Quantachrome model Nova 1000e surface and porosity analyzer. S_{BET} was obtained using the BET method and the total pore volume (V_t) was calculated at a relative N_2 pressure of $P/P_0 = 0.99$ at liquid nitrogen temperature of 77K. The BJH method was employed to determine the mesopore surface area (S_{BJH}), the mesopore volume (V_{BJH}) and the pore size distribution in the mesoporous range (2–50 nm), based on the desorption data of the isotherm.

3.3. Advanced Oxidation and Control Tests

Different advanced oxidation (UV/H₂O₂, Fenton and photo-Fenton) and control tests (photolysis, H₂O₂) were carried out. In photolysis control test, the dye solution was exposed to UVC light for 180 min and CV dye concentration was measured every 15 min. For the oxidation process, only H₂O₂ was added to the solution and the reaction of CV dye oxidation was monitored in darkness. UV/H₂O₂ was also studied by exposing the CV dye solution to UVC light and adding H₂O₂.

To evaluate the efficiency of photo-Fenton and Fenton reactions on CV dye degradation, a 200 mL borosilicate crystallizing dish reactor (shape: round, Ø = 90 mm, h = 45 mm) was filled with CV aqueous solution (V = 100 mL) and the catalyst dose. The solution was homogenized for 60 min using a magnetic stirrer in a closed chamber to ensure adsorption–desorption equilibrium at room temperature in dark, then a sample was taken for CV dye concentration control and centrifuged, filtered and analyzed using a UV-visible spectrophotometer (at λ_{max} = 583 nm). In the Fenton test, the time started when H₂O₂ was added to the aqueous solution. For photo-Fenton process, the UV-C lamp (16 W, Sankyo Denky G10T5L, Japan), placed at 10 cm from the top of the aqueous solution, was used as light source and the light intensity (4.9 mW/cm²) was measured using a radiometer (model HR-2000, Ocean Optics, Florida, USA). In a typical experiment, 0.1 g of natural iron oxide (m_{cat} = 0.1g) was steadily mixed with 100 mL of CV dye solution. Then, 3 mL of suspension was collected every 15 min. The catalyst was removed from the mixed solution by centrifugation (9000 rpm for 10 min) and subsequently filtered to perform CV spectrophotometric measurements.

In order to perform stability tests, the catalyst was recovered by centrifugation, rinsed with distilled water and dried in an oven at 60 °C for a period of 24 h. In each experiment, 0.1 g of catalyst was taken into consideration.

3.4. Analytical Measurements

COD analysis was carried out using cuvette tests (HACH Co.). BOD₅ was measured according to standard methods (CNR IRSA 5120) [55] using an OXITOP[®] system [11]. Hydrogen peroxide residual concentration was determined by reaction between Titanium oxysulfate and H₂O₂ (DIN 38 409H15 method) to produce pertitanic acid (yellow color). Then, the absorbance measurement of the complex was obtained using a Perkin Elmer UV-vis spectrophotometer at λ = 410 nm. Total suspended solids (TSS) were analysed following the CNR IRSA 2090 standard methods [55]. Turbidity values were obtained directly using a 2100AN model turbidity meter (HACH) [56]. Conductivity and pH were measured using a pH meter edge[®] (HANNA, model: HI2020-02). The CV residual concentration was analyzed using a Perkin Elmer UV-vis spectrophotometer (Model T60U PG Instruments Ltd.) through absorbance measurement at λ_{max} = 583 nm. To identify the demethylated degradation products of CV dye, an LC/MS system equipped with a binary pump, a photodiode array detector, an autosampler and a micromass detector were used. The used mobile phase was a mixture of methanol and aqueous ammonium acetate buffer (25 mM), with a flow rate of 1.0 mL/min. Analyses were performed on an Atlantis TM dC18 column (250 mm × 4.6 mm i.d., dp = 5 µm) and the column effluent was introduced into the ESI source of the mass spectrometer through a heated nebulizer probe at 350 °C and with an ion source temperature of 80 °C. The cationic and anionic by-products of the CV dye were analyzed using an Ion-Chromatograph (Metrohm) 800 series (IC), connected to an electrical conductivity detector.

4. Conclusions

In this work, natural iron oxide was characterized and used as catalyst in Fenton and photo-Fenton reactions. TEM analysis of the catalyst showed rod shape structures with a mesoporous texture. BET analysis allowed to measure a high specific surface area of the catalyst (45.8 m²g^{−1}). According to the optical characterization, the photo catalyst showed absorption in both UV and visible light regions, which makes it a good candidate

for photo-catalytic processes. The natural iron oxide was evaluated for CV dye degradation by photo-Fenton reaction and compared to Fenton and UV/H₂O₂ processes, photo-Fenton being the most effective, with almost total degradation of the CV dye under the optimum conditions (1.0 g/L of catalyst dose and 30 mg/L of H₂O₂). Additionally, regeneration experiments proved the stability and reusability of the catalyst. Finally, an application of the process on real textile wastewater revealed promising results in terms of COD, BOD₅ and TSS removals, and made the effluent in compliance with the corresponding standards set by (Italian) regulations for disposal into sewerage.

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