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Natural iron oxide as catalyst for heterogeneous photocatalysis and Fenton-like process: kinetic study

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ABSTRACT

The catalytic efficiency of a natural mineral to promote photocatalysis and Fenton-like reaction was examined by using a cationic dye, Cristal Violet (CV) as a model compound at pH 8.3. The adsorption of CV on natural iron oxide (NIO) surface was investigated from both equilibrium and kinetic point of view and the sorption isotherm was fitted using the Freundlich model. The NIO shows high photocatalytic activity in the presence of ultraviolet and solar light with CV conversion higher than 64% and 96% after 300 min of reaction respectively. The presence of hydrogen peroxide in aqueous NIO slurry produces a beneficial enhancement of the reaction rate of CV removal, leading to a heterogeneous Fenton-like reaction at pH 8.3. The effects of different parameters such as initial concentration of H_2O_2, solution pH and UV light on the decolorization efficiency of the process were studied. The results indicated that in dark Fenton-like process, the reduction of initial pH from 8.3 to pH 3.0 increases CV removals from 66.8% and 78.5%. At pH 3, the reaction is essentially a combination of heterogeneous Fenton-like process associated with typical homogeneous Fenton reaction due to the dissolution of NIO. Photo-Fenton-like oxidation leads to higher removal rate than Fenton either at pH 3 or pH 8.3. After three runs of regeneration, the activity of the catalyst shows the same efficiency in Fenton-like process. Based on the results of this study NIO may be considered as a promising material for photocatalytic water treatment.

Keywords: Natural mineral; Cristal violet; Photocalysis; Solar light; Fenton-like

1. Introduction

Wastewater treatment processes are designed to achieve improvements in the quality of the wastewater. The various treatment processes may reduce the persistent organic pollutants (POPs), that are resistant to environmental degradation through chemical, biological, and photolytic processes [1]. Many POPs are currently or were in the past used as pesticides, solvents, pharmaceuticals and industrial chemicals [1]. In particular, the disposition of colored effluents produced by textile, paper pulp, plastic and other industries represent a technological problem that affects several countries all around the world. There are several types of commercial dyes and some of these dyes possess a high resistance to biodegradation and persist a long time in the environment [2,3]. These compounds and their degradation byproducts are generally believed to be carcinogenic or toxic and become harmful to humans or to the environment where they are discarded [4,5]. Crystal Violet has been extensively used in human and veterinary medicine as a biological stain and as a textile dye in textile processing industry [6,7]. Crystal Violet has been classified as recalcitrant dye and remains in the environment for longer period. It is toxic to aquatic and terrestrial life [6,7]. Investigations on Crystal Violet in vitro concluded that this dye was a mitotic poisoning agent. It is a potent clastogenes, which is responsible for promoting tumor growth in some species of fish and also known as potent carcinogenic [6,8]. Advanced oxidation processes (AOPs) have been developed as effective technologies for the

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degradation of recalcitrant and toxic compounds found in air, water and wastewater [9,10]. AOPs are characterized by the involvement of free radicals (mainly $^\bullet OH$) that are very powerful and hence nonselective oxidants (2.8 V vs. SHE)[11]. A typical homogeneous Fenton process uses ferrous ions to activate H_2O_2 to generate $^\bullet OH$. This process require operation at low pH values (pH ≤ 3), due to the production of iron sludge at higher pH values. To overcome this drawback, chelating agents such as ethylenediamineteraaceticacid (EDTA), oxalic acid, citric acid and tartaric acid can be added in both homogeneous and heterogeneous systems to prevent the formation of iron sludge [12–14]. In heterogeneous systems iron minerals are used instead of soluble iron to produce hydroxyl radical for an efficient degradation of the organic molecules at circumneutral pH and the process is known as Fenton-like oxidation. In previous works, we have demonstrated that the combination of natural iron oxide (NIO) and oxalic acid under UV irradiation produces a strong increase in activity for the photo-Fenton like reaction [15]. Satisfactory results are obtained for the degradation of 2,6-dimethylphenol in NIO/oxalate/UV system. Another alternative process, iron oxide-catalysed Fenton, in which the abatement of the pollutants is achieved by using H_2O_2 in the presence of a specific iron oxide suspended in the treated wastewater [16,17]. In this process, iron is stabilized within the interlayer space of the catalyst's structure and can effectively produce hydroxyl radicals from oxidation of hydrogen peroxide. The process occurs under non-controlled pH conditions and without iron hydroxide precipitation as in the case of Fenton process and the catalyst can be easily recovered and re-used being practically insoluble [18]. Several heterogeneous catalysts, in pure or structurally modified forms, have been employed in Fenton reactions such as iron pillared clays [19], iron containing zeolites [20] and iron minerals [16,21,22]. In another hand, The photocatalytic degradation of organic pollutants on the surface of iron oxides is also very feasible and useful for removal of organic pollutants from contaminated soils and waters and have attracted the interest of many researchers [23,24]. The main objective of the present work is focused on the integration of photocatalysis, Fenton-like catalysis through the use of NIO asheterogeneous and natural low cost photocatalyst and H_2O_2as oxidant. A preliminary study of the adsorption and the photocatlysis of CV on NIO surface were examined. The efficiency of the catalyst was analyzed with respect to various experimental variables such pH, concentration of dye and catalyst and initial [H_2O_2]. We have noted that NIO as heterogeneous Fenton-like catalyst could activate H_2O_2 to degrade CV effectively in the darkover a wide pH range.

2. Experimental

2.1. Chemicals and materials

The NIO was washed several times with distilled water and dried at 45°C. All reagents used in this work were analytical grade and were used without any further purification. Crystal violet was purchased from Biochem, hydrogen peroxide was provided from Prolabo and sodium hydroxide (98%) by Carlo Erba Reagenti. Sodium acetate (99%) and sulfuric acid (98%) by Panreac; silver sulfate and 1,10-phenanthroline (>99%) by Fluka. Perchloric acid (60%) was from Merck. All solutions were prepared in Milli-Qwater (Millipore).

2.2. Experimental procedures

The oxidation experiments were performed in a Pyrex cylindrical reactor with a double envelope was placed in the centre of a cylindrical aluminium container. The suspensions of CV (6 ppm) and 1 g L^{-1} of iron oxide were stirred in the dark for 30 min to establish adsorption/desorption equilibrium. After that the required volume of H_2O_2 was then added. In the photo-oxidation experiments, the reactor was exposed to the radiation sources composed of a fluorescent lamp (Philips TLAD 15W/05), which dominantly emits radiation at 365 nm. Light intensity (I = 0.45 mW cm^{-2}) was measured using a radiometer type VLX 3W. The solution was continuous magnetically stirred during experiments to insure its homogeneity. The samples withdrawn at different reaction times were filtered with cellulose acetate filters (0.45 µm) to separate NIO particles. All experiments were performed at T = 20 ±2°C by cycling water. The solution pH was adjusted by 1.0 M of $HClO_4$ or NaOH and measured by means of an HANNA Instruments 8521 pH-meter. The tests under natural solar radiation were carried out during sunny days in Constantine, Algeria (latitude 36°20'N, longitude 6°37'E). Experiences were conducted in a cylindrical Pyrex reactor, placed vertically. Light intensity was 0.98 W cm^{-2} measured with a solar light radiometer PMA2100 positioned to sample height.

2.3. Analytical methods

The concentrations of the residual CV were determined by monitoring decrease in absorbance at the maximum wavelength (592 nm) employing a Thermo scientific spectrophotometer controlled by software « Thermo INSIGHT ».The Fe(II) leached from NIO into the reaction solution was determined by using the 1, 10-phenanthroline method. Low dissolved iron concentration was detected in the solution.

3. Results and discussion

3.1. Properties of material

The NIO used in this study was obtained from the iron deposits which is located in North-East Algeria. The collected powder was washed and dried at 45°C before using for oxidation treatment. The XRD patterns showed that the mineral has a mixed crystal structure composed mainly of hematite with 9 characteristic peaks of hematite. The results of BET show that the NIO had the specific surface area equal to 79.015 m^2 g^{-1} and total pore volume of 0.0892 $cm^3 g^{-1}$. (Detailed analysis has been already published in our previous studies [15]).

3.2. Adsorption kinetics of CV on NIO surface

The affinity of the catalyst surface for pollutant molecules is considered as an important factor for photocatalytic degradation efficiency. In this purpose, we studied the adsorption of CV on the NIO surface. The kinetic studies were carried out at different initial concentrations of CV with the concentration of NIO of 1.0 g L^{-1} and at pH 8.3. Fig. 1 shows the variation of the amount adsorbed (Q_{ads})

of CV versus reaction time. The results presented indicate that the rate of adsorption increased when CV concentration increased. Most of adsorption proceeds within the first minutes for all concentrations which show that the rate of dye adsorption by NIO particles is high.

The curve obtained by plotting at constant temperature the amount of adsorbate (Q_e) against the residual concentration of the substance at the equilibrium (C_e) is known as the adsorption isotherm. It describes how adsorbate interacts with sorbent materials. The adsorption isotherm of CV on NIO is presented in Fig. 2. The results indicate that the adsorption of CV on NIO increased with C_e. Initially, the amount adsorbed increases rapidly and then becomes more moderate at the average values of C_e, and then returns to increase at high values of C_e. Based on the Brunauer, Deming and Teller (B.D.T) classification, this adsorption is of type II, the adsorption is carried out in multilayers at the high concentration values after the saturation of the surface by a monolayer. The equilibrium data was modeled with Langmuir (Eq. (1)) and Freundlich (Eq. (2)) models.

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{K_L.Q_m} \times \frac{1}{C_e} \tag{1}$$

$$LnQ_e = LnK_f + \frac{1}{n_f} LnC_e \tag{2}$$

The adsorption parameters obtained with these models are shown in Table l. According to the results, the adsorption of CV on NIO can be better fitted by Freundlich model than by Langmuir model. The Freundlich constant n_f informs us about the heterogeneity of the surface, for $n_f > 1$ we have a physisorption [25]. In our case $n_f = 5.40$, thus we have a physisorption which confirms the adsorption of type II.

3.3. Photocatalytic activity of the catalyst

The photocatalytic activity of the catalyst was examined by the decomposition of CV dye under UV illumination (Fig. 3). Preliminary experiment performed in the absence of catalyst (i.e. photolysis) verified that the dye isresistant to self-photolysis as the energy of 365 nm is too low to degrade dye molecule. However, the removal percentage of CV under solar irradiation was 47.2% after 300 min. CV may absorbs both the UV and visible parts of the solar spectrum. In addition, the rate adsorption of CV onto catalyst surface was found to be, after 30 min of magnetic stirring, about 55% degradation (t = –30 min, corresponds to adsorption). The irradiation of (CV-NIO) suspension at 365 nm and with solar light caused 64.3% and 96% of decolorisation of CV dye after 300 min of reaction respectively. Those removal percentages are related to the synergy of adsorption and photocatalysis in presence of NIO. The NIO particles showed excellent photo-sensitized degradation of CV dye under solar irradiation. Irradiation of iron oxide suspension with UV or solar light, exceeding the semiconductor band gap energy, generates an electron/hole pair. Therefore, CV may be oxidized by positive hole, hydroxyl radical and reduced by electron in the conduction band.

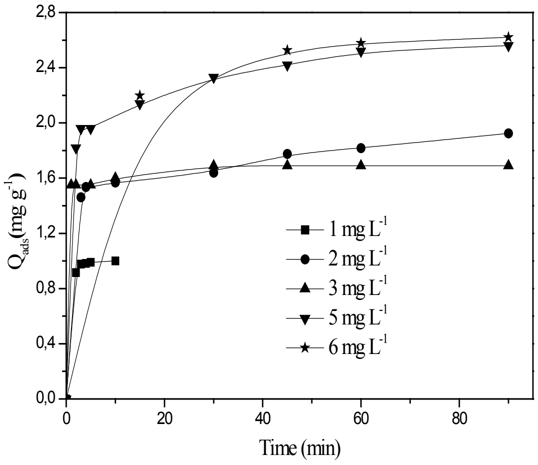

Fig. 1. Experimental kinetics for the adsorption of CV by NIO at different initial concentrations, [NIO] = 1 g L^{-1}; pH = 8.3.

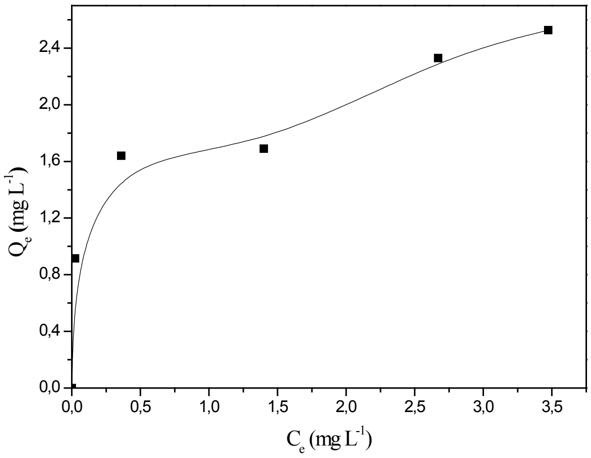

Fig. 2. Adsorption isotherm of CV on NIO surface. [NIO] = 1 g L^{-1}; pH = 8.3.

Table 1
Isotherm parameters for the adsorption of CV onto NIO particles

Langmuir			Freundlich		
Q_m	K_L	R^2	K_f	n_f	R^2
2.03	35.7	0.88	1.84	5.40	0.923

3.3.1. Photocatalytic oxidation

The Reactions for the photocatalytic oxidation of organic compounds under UV light in presence of iron oxides are as follows. First, photosensitization of the CV dye takes place where charge transfer occurs from the LUMO level of the dye to the conduction band of the photocatalyst [Eqs. (3) and (4)]. This is followed by the light absorption by the natural hematite (α-Fe_2O_3), when photons with energy(hn) equal to or greater than the semiconductor bandgap (Eg) are incident, electrons

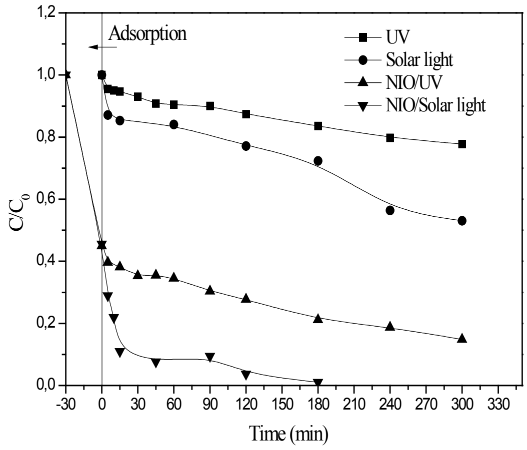

Fig. 3. Photolysis and photocalysis of CV (6 mg L^{-1}) in presence of NIO (1 g L^{-1})under UV and solar irradiation.

(e_{cb}^-) and holes (h_{vb}^+) are generated in the conduction and valence band, respectively [26,27] [Eq. (5)]. Then the excited electrons and holes separate and act as reducing and oxidizing agents, respectively, to produce hydroxyl radicals ($^{\bullet}OH$). Oxygen is present to act as the primary electron acceptor; electron transfer to oxygen may be the rate-limiting step [28]. The superoxide radicals ($O_2^{\bullet-}$) are generated by photogenerated electron of α-Fe_2O_3 by reacting with chemisorbed oxygen on the catalyst surface and oxygen in the aqueous solution [Eq. (7)]. The reaction between superoxide radicals ($O_2^{\bullet-}$) and dissociated water (H^+) form hydroperoxyl radicals ($HO_2^{\bullet}$) (Eq. (8)). The dismutation of hydroperoxyl radicals forms H_2O_2 [Eq. (9)]. The holes are scavenged by surface hydroxyl groups [formed by adsorbed water Eq. (6)] to generate strong oxidizing hydroxyl radicals ($^{\bullet}OH$) [Eq. (10)]. These reactive radicals and intermediate species are able to degrade CV and a large variety of organic compounds (toxic and non-toxic) and biological agents [29,30]into non-toxic mineral compounds Eq. (11).

$$CV + h\nu \rightarrow CV^{\bullet} \tag{3}$$

$$CV + \alpha\text{-}Fe_2O_3 \rightarrow CV^{\bullet} + \alpha\text{-}Fe_2O_3(e_{cb}^-) \tag{4}$$

$$\alpha\text{-}Fe_2O_3 + h\nu \rightarrow \alpha\text{-}Fe_2O_3(e_{cb}^- + h_{vb}^+) \tag{5}$$

$$H_2O \rightarrow H^+ + OH^- \tag{6}$$

$$e_{cb}^- + O_2 \rightarrow O_2^{\bullet-} \tag{7}$$

$$O_2^{\bullet-} + H^+_{aq} \rightarrow HO_2^{\bullet} \tag{8}$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{9}$$

$$h_{vb}^+ + OH^-_{surface} \rightarrow {}^{\bullet}OH \tag{10}$$

$$CV^{\bullet}/CV^{\bullet+} + (O_2^{\bullet-}, HO_2^{\bullet}, H_2O_2, {}^{\bullet}OH) \rightarrow \text{Degradation products}\ldots \tag{11}$$

3.3.2. Effect of catalyst loading

For economic removal of dye effluent from wastewater, it is necessary to find the optimum amount of catalyst for efficient degradation. Several authors have studied the reaction rate as a function of catalyst loading in photocatalytic oxidation process [31]. To investigate the relationship between the catalyst loading and the degradation rate of the dye, the amount of NIO varied from 0.5 to 1.5 g L^{-1} in a series of experiments at constant conditions: dye concentration is 6 mg/L, pH = 8.4 and reaction temperature is 20°C. It is important to note that degradation of CV started 30 min before illuminating the reactor (adsorption) with removal percentage of 42.7%, 55%, and 60.5% for 0.5, 1.0 and 1.5 g L^{-1} respectively. Fig. 4 shows that, after illumination, when the amount of the catalyst increased the decolorization efficiency went up first, this is due to increase in the number of Fe_2O_3 particles, which increases the number of photons absorbed, enhancing generation of $^{\bullet}OH$ radicals and leading to faster degradation of CV. But when the amount exceeded 1 g L^{-1}, we have not noticed an improvement in the degradation of CV. However, an excessive iron oxidedose may cause light scattering and screening effects. These reduce the specific activity of the catalyst [32]. Hence, starting from an economic point of view, 1.0 g/L of NIO loading was selected to be the optimal loading assayed for maximum efficiency. These kinetic curves (after adsorption) can be approximated as a pseudo-first-order process which allowed us to determine the rate constant (k) and thus to quantitatively compare the efficiencies of the different doses of catalyst under similar experimental conditions. The rate constants (k) were determined to be 1.43 × 10^{-3} mn^{-1} (R^2 = 0.92), 3.19 × 10^{-3} mn^{-1} (R^2 = 0.98) and 2.05 × 10^{-3} mn^{-1} (R^2 = 0.94) for 0.5, 1.0 and 1.5 g L^{-1} respectively.

3.3.3. Effect of dye concentration

The effect of various initial dye concentrations on the photocatalytic decolorization have been investigated over a concentration range of 4 mg L^{-1}–10 mg L^{-1} of CV and with the optimal concentration of NIO of 1.0 g L^{-1}. The removal percentages of CV after adsorption were 59%, 55% and 25% for 4, 6 and 9 mg L^{-1}. Fig. 5 shows that the rate of photocatalytic degradation decreased with increasing the initial concentration of CV. Increase in the concentration of dye from 4 to10 mg L^{-1} decrease the decolorization from 83% to 42%, in 180 min. Similar results have been reported for the photocatalytic oxidation of other dyes [33,34]. When the dye concentration increases the amount of dye adsorbed on the catalytic surface increases. This affects the catalytic activity of NIO. The increase in dye concentration also decreases the path length of photon entering into the dye solution. At high dye concentration a significant amount of UV-light may be absorbed by the dye molecules rather than the catalyst and this may also reduce the catalytic efficiency [35].

3.4. Fenton-like oxidation of CV in the presence of NIO

Fig. 6 shows the results of a set of experiments performed in the dark by adding, respectively, H_2O_2 (5 mM), NIO (1 g L^{-1}) and both of them to CV (6 mg L^{-1}) aqueous solutions. As it can be seen, H_2O_2 in the dark was not able to

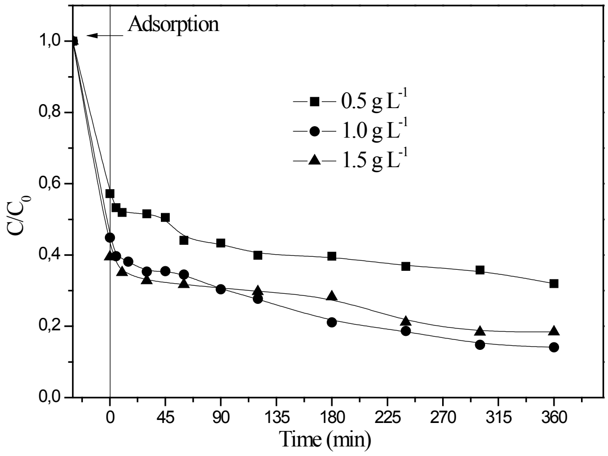

Fig. 4. CV photodegradation rate under different catalyst loading [CV] = 6 mg L^{-1}, pH = 8.4, T = 20°C.

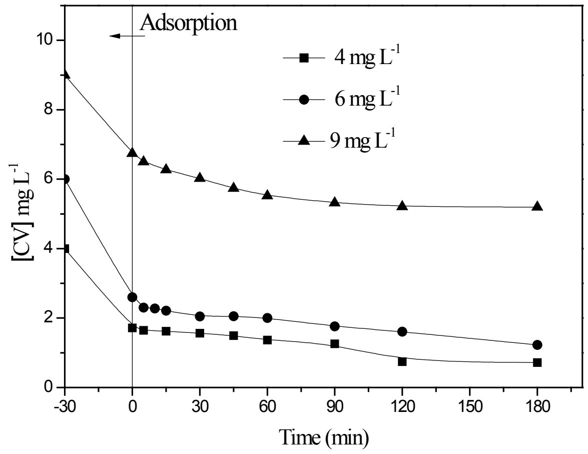

Fig. 5. Effect of various dye concentrations on the phodegradation of CV [NIO] = 1 g L^{-1}, pH = 8.4, T = 20°C.

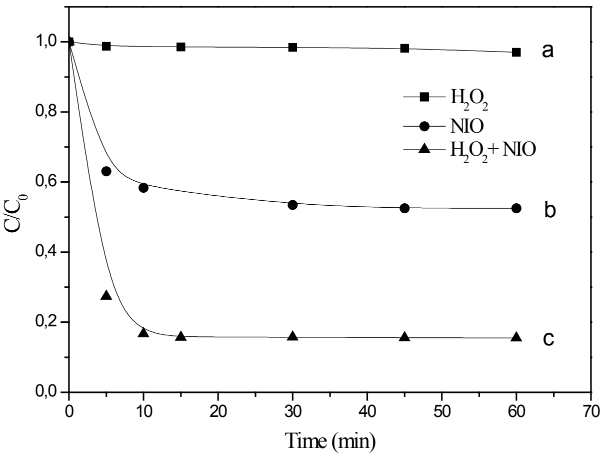

Fig. 6. Oxidation of CV in different systems, (a) H_2O_2, (b) NIO, (c) NIO + H_2O_2. Reaction conditions: [CV] = 6 mg L^{-1}, [H_2O_2] = 5 mM, NIO load 1 g L^{-1} pH = 8.3.

degrade CV. The oxidizing power ($E^0 = 1.78$ V) of hydrogen peroxide may be not enough for direct oxidation of CV. For adsorption process using NIO, the decolorization rate was 55% as see precedly. The removal of CV within 60 minutes was 85%for the NIO and H_2O_2 combination system. Such an enhancement in color removal may be ascribed to the synergy of adsorption by NIO and heterogeneous Fenton oxidation reaction catalyzed by NIO. Therefore, NIO particles promote the activation of H_2O_2 in the dark and at natural pH (equal to 8.3).

The action of H_2O_2 on the oxide surface can transform the oxide particles into an only Fe^{III}-bearing mineral or into an amorphous iron oxide which may be less stable and more soluble [17]. This mineralogical transformation may lead to a substantial change in the surface characteristics of the mineral, causing a different kinetic behavior and decomposition rate for H_2O_2 [17]. The Fenton-like catalytic ability of iron oxide particles for the degradation of organic pollutants in the presence of H_2O_2 in the dark originated from its enhancing effect on the generation of hydroxyl radicals [36,37]. A mechanism to explain the formation of $^{\bullet}OH$ radicals on the surface of iron oxides has been proposed [38]. First, hydrogen peroxide is adsorbed on the surface of the iron oxides leading to the formation of $\equiv Fe^{3+}$ - H_2O_2 complex (Eq. (12)), which is followed by the reduction of ≡Fe(III) to ≡Fe(II) (Eq. (13)). The reaction between the ≡Fe(II) on the surface and H_2O_2 generate $^{\bullet}OH$ radicals (Eq. (14)).

$$\equiv Fe^{3+} + H_2O_2 \rightarrow \equiv Fe^{3+} - H_2O_2 \quad (12)$$

$$\equiv Fe^{3+} - H_2O_2 \rightarrow \equiv Fe^{2+} + HO^{\bullet}_2 + H^+ \quad (13)$$

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+} + {}^{\bullet}OH + OH^- \quad (14)$$

3.4.1. Effect of H_2O_2 dose on decolorization rate of CV

The effect of H_2O_2 concentrations on CV degradation in NIO/H_2O_2 system was investigated and shown in Fig. 7. The figure shows the photocatalytic degradation of CV (6 mg L^{-1}) with NIO (1 g L^{-1}) in the presence of H_2O_2at different concentrations ranging from 10^{-3}–10^{-2} M.

It can be seen that the CV degradation occurs in two stages a fast first-stage reaction and a slow second-stage reaction. In the first-stage, the highest rate of CV degradation was observed in the initial five minutes of the reaction for all concentrations, which corresponds to the fast decomposition of H_2O_2. The decolorization of CV solution is directly related to the concentration of the hydroxyl radicals produced by the catalytic decomposition of hydrogen peroxide. In the slow second-stage, the appearance of a bearing explains the relationship of CV degradation and consumption of H_2O_2. The removal of CV increased from 55% to 99% with the increase of hydrogen peroxide concentration from 10^{-3} M to 10^{-2} M after 60 min of reaction. More CV decomposition is expected when hydrogen peroxide dosage increases; implying that the number of sites on iron oxide surface available for adsorption of hydrogen peroxide was still not limited. However, under the range of hydrogen peroxide concentration used in this study, the scavenging effect [Eq. (15)] of $^{\bullet}OH$ was not observed as expected in Fenton and

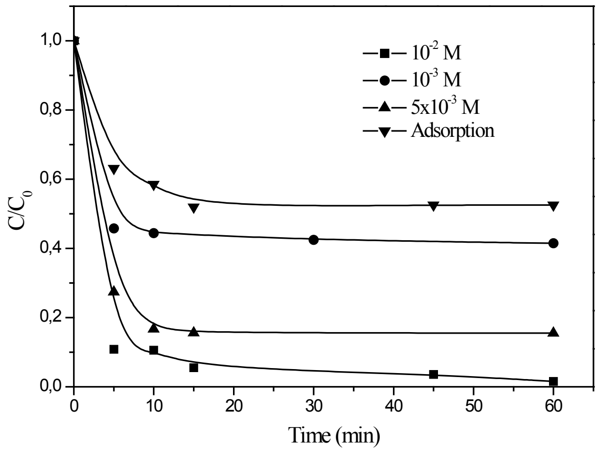

Fig. 7. Effect of H_2O_2 concentrations on CV degradation in NIO/H_2O_2 system [CV] = 6 mg L^{-1}, NIO load 1 g L^{-1} pH = 8.3.

like – Fenton processes [39]. At low H_2O_2 concentration, the •OH radicals preferentially attack the substrate molecules, whereas at higher H_2O_2concentration, there is a competitive reaction between the substrate and H_2O_2. Thus, the dosage of hydrogen peroxide should be adjusted in such a way that the entire amount is utilized because excess amount is harmful to many organisms [40]and will affect the overall degradation efficiency by scavenging effect.

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \text{ [k = 1.7 – 4.5 } 10^7 \text{ M}^{-1} \text{ s}^{-1}\text{[39]] (15)}$$

3.4.2. Effect of pH and UV light in NIO/H_2O_2 system

The photo-Fenton-like system is generally accepted to be active within a wide pH range (2.0–7.0) with an optimum value at around pH 3.0 [41]. In our system (NIO/H_2O_2/UV) the reaction occurred even at pH = 8.3. The effect of decreasing the initial pH from 8.3 to pH 3.0 on CV removal rates is displayed in Fig. 8a. The experimental conditions were 1 g L^{-1} of NIO and 5.0 mM of H_2O_2. The result showed that CV was rapidly transformed during the dark Fenton-like reaction within 5 min after hydrogen peroxide was added. We noted 66.8% and 78.5% of degradation at pH = 8.3 and pH = 3.0 respectively after 120 min of reaction. Once UV radiation started to enter the reactor, CV removal increased slightly from 66.8% to 77% and from 78.5% to 95% during 120 min of treatment for pH = 8.3 and pH = 3.0 respectively.

At acidic pH, iron was released to the solution leading to a combination of heterogeneous and homogeneous Fenton degradation process [Reactions (14) and (16) respectively].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \quad (16)$$

While the Fenton system is able to generate •OH radicals by those reactions, the presence of UV light (photo-Fenton) contributes to the formation of •OH as well as to maintaining of Fe^{2+} in solution by Reaction (17):

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (17)$$

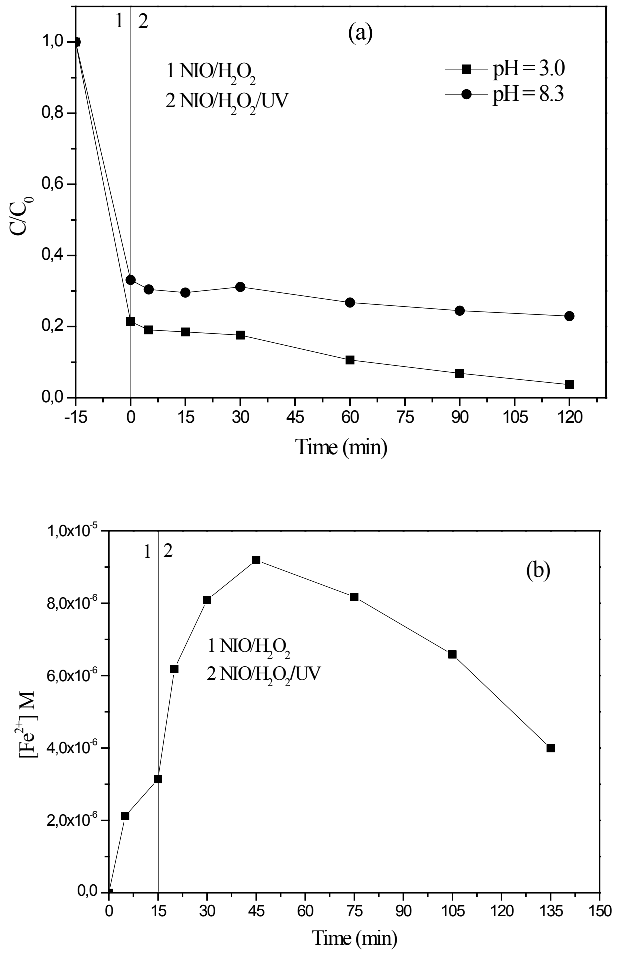

Fig. 8. Effect of pH and UV light in NIO/H_2O_2 system (a), formation of Fe^{2+} in NIO/ $H_2O_2$and NIO/ H_2O_2/UV at pH = 3.0 (b).

The newly generated ferrous ions react with H_2O_2 and generate hydroxyl radical and ferric ion, and the cycle continues. $Fe(OH)^{2+}$ molar absorptivity is higher (1535 M^{-1} cm^{-1} at 320 nm, 560 M^{-1} cm^{-1}at 350 nm and 35 M^{-1} cm^{-1} at 400 nm [42]) than the molar absorptivity of hydrogen peroxide at wavelengths >320 nm (e_{H2O2} < 0.24 M^{-1} cm^{-1} [43]). So, the photolysis of H_2O_2 hardly takes place in the studied system.

The combination of Fenton reaction with conventional radiation zone of the visible and near ultraviolet gives a better degradation of organic pollutants [44].

The acid medium causes the dissolution of the iron oxide, Fe^{2+} dissolved from NIO, was also measured by assaying with 1-10-phenanthroline (Fig. 8b). According to Eq. (16), •OH radicals were produced and Fe^{2+} was oxidized to $Fe^{3+}$and gradually consumed.

3.5. Catalytic stability and reusability of NIO

The reusability of NIO was evaluated by successive batch experiments of CV (6 mg L^{-1}) degradation in the NIO-H_2O_2 (1 g L^{-1}–5 mM) system in the dark at pH = 8.3. The catalytic stability test has been investigated under identical

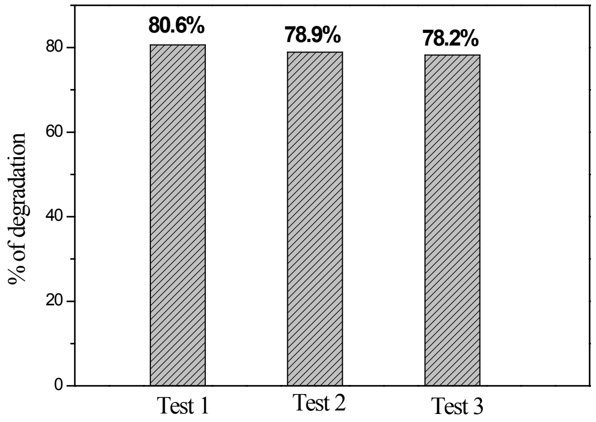

Fig. 9. Dye removal percentage by the reused catalyst in Fenton-like system [CV] = 6 mg L^{-1}, [H_2O_2] = 5 mM, [NIO] = 1 g L^{-1}, pH = 8.3.

reaction conditions. At the end of the oxidation process, the solid is easily removed from the reactor and dried at moderate temperature (45°C). The dried catalyst was added to another batch of reaction solution containing CV and hydrogen peroxide. The concentrations of CV measured during the stability test are compared in Fig. 9. It was found that the solid was able to be reused for at least three cycles, and the removal percentage after one hour of reaction for the CV degradation was estimated to be 80.6%, 78.9% and 78.2% for the three cycles respectively. The excellent stability of the catalytic activity could be attributed to the low loss of iron content during oxidation cycles and to the structural stability of the solid [17,45]. The reused catalyst retained catalytic activity practically as efficient as fresh material, so, it may be concluded that NIO could be recycled effectively.

4. Conclusion

A natural iron oxide has been used as an effective adsorbent to remove intrinsically cationic dye from aqueous solutions. The equilibrium adsorption studies show that Freundlich model was best fitted to the equilibrium data which indicate that the surface is heterogeneous. The results show that the NIO can efficiently catalyze the decomposition of CV in the presence of UV light. The use of sunlight as a source of energy for the degradation process has yielded 96% of decolorisation of CV dye after 300 min of reaction. Hematite has the advantage of low band gap and using the visible light for its photocatalytic reactions. NIO particles are capable to catalytically activate $H_2O_2$for the degradtion of CV in the dark and at pH 8.3, yielding to heterogeneous Fenton-like process. The removal rate of cationic dye by Fenton-like oxidation increased with the dosage of H_2O_2 and UV light. At pH 3.0 both heterogeneous photo-Fenton-like process and Fe leaching from the NIO surface happened for the degradation of CV. The NIO catalyst exhibited good stability and no loss of performance in third reaction cycle. The results of this study indicate that the combination of adsorption on NIO followed by advanced oxidation, photocatalysis and Fenton process is a promising process for the removal of organic contaminant from aqueous solutions.

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