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Mineralization of Acid Green 50 by Fe_2O_3–Al_2O_3 as a highly active hetero-Fenton catalyst

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ABSTRACT

The oxidation of Acid Green 50 (AG50) textile dye using Fe_2O_3–Al_2O_3, prepared from the calcination of Fe^{III}–$Al(OH)_4$-gel, as a highly active catalyst in the heterogeneous Fenton oxidation process was studied. It was found that the ferric ions loaded on the surface of neutral $Al(OH)_4^-$ gel and then calcined at different temperatures is an efficient catalyst in the heterogeneous Fenton reaction for the mineralization of aqueous AG50. According to the X-ray analysis, the iron catalyst is a mix of Fe_2O_3 and Al_2O_3. The thermal treatment gives long-term stability to the catalyst because it minimizes iron leaching from the catalyst. The catalyst was used in four successive recycling heterogeneous Fenton oxidations generating a colorless solution with the removal of over 95% of total organic carbon (TOC) in 90 min. This shows that the Fe_2O_3–Al_2O_3 catalyst is highly efficient for the degradation of AG50 after being used in several cycles during the dye treatment. It was also found that the degradation of AG50 increased by increasing the hydrogen peroxide concentration.

Keywords: Acid Green 50; Fe_2O_3–Al_2O_3; Fe^{III}–$Al(OH)_4$-gel; Heterogeneous Fenton

1. Introduction

The release of dye compounds from the dyeing and finishing operations into textile effluents has become a major concern, since many dyes remaining in the residual waters are toxic and can also have carcinogenic and mutagenic effects [1,2]. In addition to the heavy color, that imparts nonesthetic visual impact, the textile wastewaters contain heavy metals (associated with some of the dyes), high chemical oxygen demand, suspended solids, and low biodegradable chemicals especially the effluent from the dyeing and finishing processes [3–5]. The worldwide environmental regulations have become more stringent towards wastewater discharges demanding efficient

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and environmental friendly treatment technologies. Advanced oxidation processes (AOP) are considered as nonwaste generating technologies, and represent an alternative wastewater treatment for dye effluents when common wastewater treatment technologies are ineffective [6–8]. AOP have been proposed as complementary technique for polishing treated water, when contaminants are resistant or toxic to conventional biological treatments, and as disinfection and deactivation of pathogenic micro-organisms that are difficult to degrade biologically [9–13]. The AOP have in common the production of hydroxyl radicals, ·OH, considered as highly reactive oxidizing species. Among these AOP, the Fenton reaction offers an environmental friendly alternative and cost-effective source of these nonselective oxidizing species that are responsible for the mineralization of organic pollutants present in mildly acidic aqueous effluents [14–16]. Nevertheless, some limitations for using the homogeneous Fenton process have been reported such as the catalytic activity ceases after certain time because the iron undergoes chemical speciation in the Fenton process [15–18], formation of sludge during post-treatment process, and high iron loss to the environment [19,20]. Based on these drawbacks several heterogeneous catalysts have been developed and used for the oxidation of wastewater pollutants in the Fenton-like process [21–28]. The main advantages of the Fenton-like process are the easy recovery of the heterogeneous catalyst at the end of the treatment and the possibility of using wider pH range in aqueous effluents during the oxidation of pollutants using this heterogeneous process [19,27]. Iron has been incorporated into porous supports of metal oxide surface such as TiO_2, Al_2O_3, and CeO_2 [22,28–31], synthetic zeolites [32], pillared clays [25], and laponite and bentonite clay-based Fe-nanocomposites [33], among others. Various iron compounds, such as Fe(0), Fe_2O_3, Fe_3O_4, and $FeHO_2$ have been reported to promote the heterogeneous Fenton reaction for the oxidation of organic compounds [34].

The aim of this study is to assess the catalytic performance of iron supported on $Al(OH)_4^-$-gel, prepared by mixing ferric ions with aluminum basic solution left over after hydrogen generation, on the heterogeneous Fenton oxidation of Acid Green 50 textile dye under the influence of several parameters.

2. Experimental

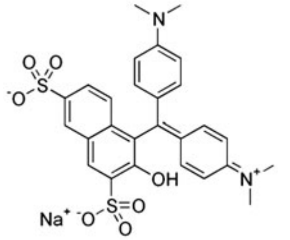
2.1. Materials

Sodium hydroxide, hydrochloric acid, nitric acid, sulfuric acid, hydrated ferric chloride, and hydrogen peroxide solution (30%) were purchased form Sigma-Aldrich. The Acid Green 50 dye (AG50) was provided by the local textile industry (Table 1). All reagents were of analytical grade and used without further purification. Total iron determination and total organic carbon (TOC) analyses were carried out using standard reagents and standard methods. Aluminum foil, from soft drink empty cans, was used after sulfuric acid treatment.

2.2. Support preparation

The lid and bottom of the aluminum cans were cut off and the rest was submerged into concentrated

Table 1
Properties of Acid Green 50

Parameter	AG50
Commercial name	Acid Green 50
Synonyms	Lissamine Green B and Wool Green S.
Chemical classification	Triarylmethane anionic dye (derivates of triphenyl methane)
Color index	C.I. 44090
Chemical formula	$C_{27}H_{25}N_2O_7S_2Na$
Molecular weight	576.61 g mol L^{-1}
λ_{max}	615 nm
Molecular structure	

sulfuric acid during 30 min to eliminate the paint and plastic film. It was followed by rising with tap water, drying with paper tissue, and cutting into small pieces. One gram of aluminum bits was added to 50 mL of 4 mol L^{-1} NaOH solution until the aluminum was completely dissolved forming an aluminum hydroxide salt and H_2 evolved according to the following reaction [35]:

$$2Al + 2NaOH + 6H_2O \rightarrow 2NaAl(OH)_4 + 3H_2 \quad (1)$$

The solution of the aluminum hydroxide salt was filtered and used for catalyst preparation.

2.3. Catalyst preparation

Calcined Fe^{III}–$Al(OH)_4^-$-gel catalysts were prepared by mixing the filtrated solution of the aluminum hydroxide salt with Fe^{3+} acidic solutions using ferric chloride as precursor salt. The iron solutions were prepared by adding a fixed amount of $FeCl_3{\cdot}6H_2O$ (Fe^{III} content of 0.1 g) in 50 mL H_2SO_4 solution (4.0 mol L^{-1}). Then each iron acidic solution was added by consecutive dropwise addition to a stirred solution of basic aluminum hydroxide thus forming a brownish aluminum hydroxide gel impregnated with iron (Fe^{III}–$Al(OH)_4^-$-gel) thereby neutralizing the aqueous solution. The product was filtered, washed with distilled water repeatedly to remove Na^+, Cl^-, and SO_4^{2-} ions, dried in an oven at 105˚C for 12 h, and grounded to powder using an agate mortar. Then powders were calcined at 300, 450, and 550˚C for 6 h under air atmosphere. A catalyst without iron only was prepared as the catalyst support (a white $Al(OH)_4^-$-gel) by neutralizing the aluminum hydroxide solution with H_2SO_4 (4.0 mol L^{-1}) following the same procedure.

2.4. Experimental procedure

A stock solution of AG50 (10×10^{-3} mol L^{-1}) was prepared with distilled water. Dilutions were prepared depending on the desired textile dye concentration (7.5×10^{-5}–10×10^{-3} mol L^{-1}) followed by additions of H_2O_2 (0–0.71 mol L^{-1}) and catalyst (100 and 500 ppm) at constant pH (3–10). Several experiments were carried out employing 100 mL. Samples were withdrawn at selected time intervals and filtered through a 0.45 μm membrane. The solution pH of the samples was raised to 11 to quench the oxidation and avoid further generation of hydroxyl radicals using NaOH solution [24]. Then sample analyses were carried out by measuring the absorbance at 615 nm (UV–vis spectrophotometer, DR-2500 Hach) and TOC. TOC was analyzed using standard methods and standard tubes inside with the concentration range of 0–40 mg L^{-1} (Hach), and a Shimadzu-VCS_N TOC analyzer calibrated with standard solutions of potassium phthalate. The iron loading on the catalyst was measured using the FerroVer standard reagent after dissolution in aqua regia (a mixture of hydrochloric acid and nitric acid). Scanning electron microscopic (SEM) analyses (LEO 1450VP) with EDX probe for the energy dispersive X-ray microanalysis (EDX) were carried out on the calcined Fe^{III}–$Al(OH)_4^-$-gel catalysts. X-ray analyses were also carried out (Rigaku X-ray diffractometer with a CuKα radiation). The mineralization efficiency (*Ef* (%)) of AG50 was evaluated using Eq (2):

$$Ef(\%) = \frac{TOC_o - TOC_t}{TOC_o} \times 100 \quad (2)$$

where TOC_o and TOC_t represent the TOC content of the AG50 solution before treatment and at sampling time during treatment, respectively.

3. Results and discussion

3.1. Characterization of catalyst

The microstructural features of iron–Fe^{III}–$Al(OH)_4^-$ gel dried at 105˚C and calcined at different temperatures (300, 450, and 550˚C) are shown in Fig. 1. The micrographs presented in Fig. 1(a) and (b) have many aggregated submicron-sized particles. Larger sized particles are also present and have nonuniform size and shape with porous structure. The iron–Fe^{III}–$Al(OH)_4^-$ gel thermally treated micrographs, presented in Fig. 1(c) and (d), have micron-sized particles with intergranular pores. The particles are more defined and have nearly uniform size with elongated and rounded shape. There are also larger sized particles with oval shape. The thermal treatment produced larger sized particles with porous structure with nearly uniform size and shape. Table 2 reports the chemical elements present in iron–aluminum gel powders with temperature. It is observed that elemental carbon is present in the catalyst since the catalyst particles were fixed on a carbon surface during the analysis but it is not part of the catalyst; also, the carbon values are not constant since they depend on the thickness of the analyzed particle. Iron–aluminum gel when dried has higher iron content than that calcined at 300 and 450˚C; also, the iron content increased as the calcination temperature increased inside the temperature range of 300–550˚C. The presence of oxygen

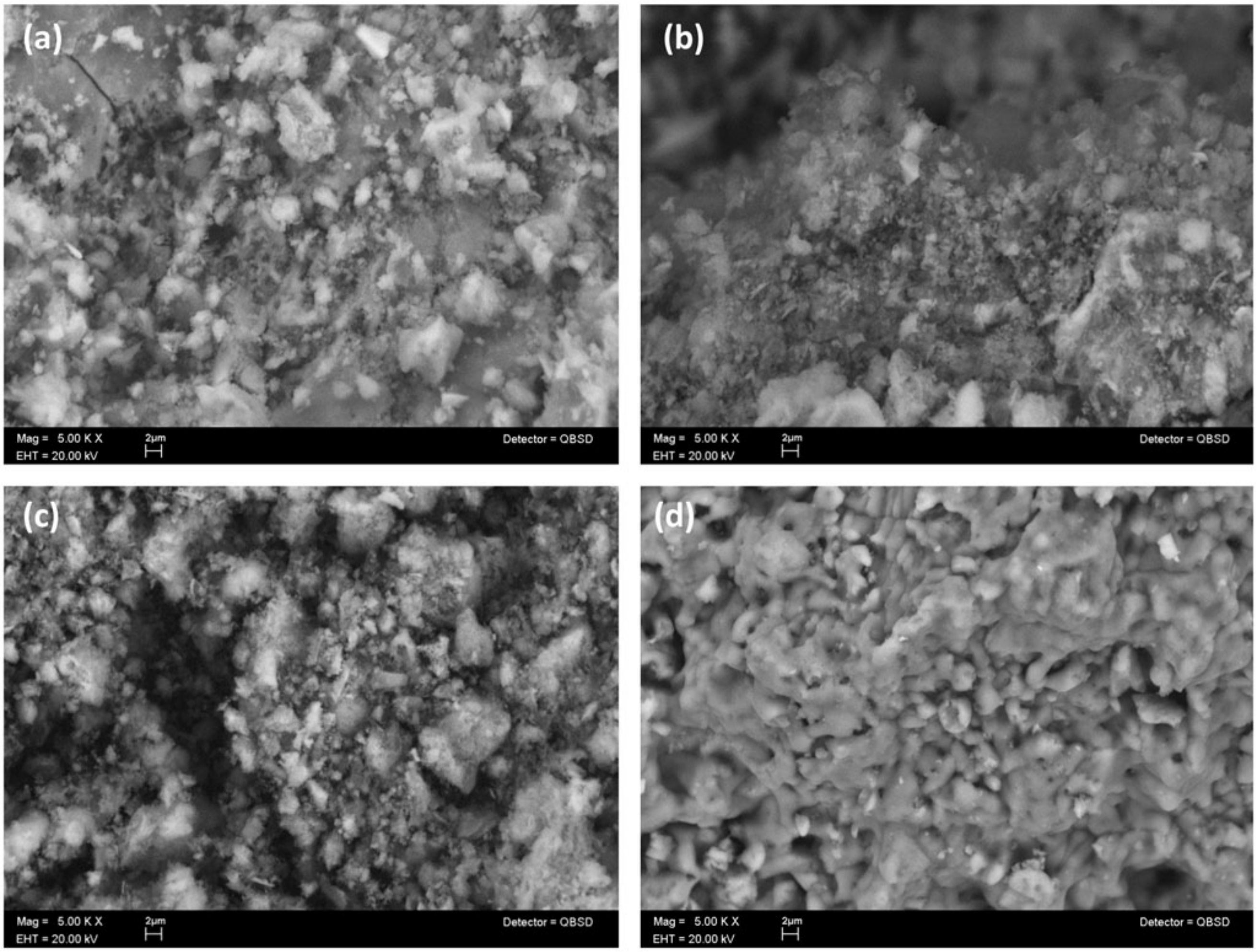


Fig. 1. SEM picture of the iron–$Al(OH)_4^-$ gel: (a) dried at 105℃, (b) calcined at 300℃, (c) calcined at 450℃, and (d) calcined at 550℃.

Table 2
Percentage of the elements (%w/w) detected on a particle of the analyzed catalysts by SEM and EDX

Element	105℃	300℃	450℃	550℃	Al 450℃
C	7.39	38.39	32.94	10.81	7.23
O	64.01	52.25	49.63	64.29	44.51
Na	6.82		6.17		1.73
Al	16.63	8.49	7.54	20.80	25.08
S	4.35	0.82	3.09	1.78	
Fe	0.80	0.60	0.64	1.81	

is an indicator of a possible formation of Fe_2O_3–Al_2O_3 oxides. The presence of sodium and sulfur in the catalyst is because Na^+ and SO_4^{2-} ions were not completely eliminated by the washing procedure with distilled water. Finally, the variation in aluminum content in the catalyst may be explained by the way it reacted with the sodium hydroxide previous to form the aluminum gel; sometimes there were small aluminum pieces attached to plastic bits that remained after the acid treatment process for paint and plastic film elimination as its content in the catalyst does not follow an increasing trend with temperature.

3.2. Catalytic mineralization of AG50

AG50 is a triarylmethane anionic dye and its oxidation involves color removal and mineralization (complete conversion to CO_2, H_2O and mineral acids). According to Eq. (3), 71 mol of H_2O_2 are required to oxidize 1 mol of AG50 in the heterogeneous Fenton reaction. Nevertheless, this equation is approximated because the atom of nitrogen has several oxidation states,

$$C_{27}H_{25}N_2NaO_7S_2 + 71H_2O_2 \rightarrow 27CO_2 + 2H_2SO_4 + NaNO_3 + HNO_3 + 81H_2O \tag{3}$$

The initial amounts of H_2O_2 used were chosen based on Eq. (3), and a systematic study was carried out to investigate the catalytic activity of Fe_2O_3–Al_2O_3 catalysts in the heterogeneous Fenton reaction for the degradation of AG50 in aqueous solution under different experimental conditions.

3.2.1. Influence of H_2O_2 concentration and calcination temperature of catalyst

Fig. 2 shows the TOC removal as a function of the concentration of hydrogen peroxide in the heterogeneous Fenton reaction. It also shows a comparison of the heterogeneous Fenton reaction with that of homogeneous system (curve g) using the same amount of iron (as Fe^{2+}) present in heterogeneous catalyst. It is clearly observed that the homogeneous Fenton process is faster than the heterogeneous Fenton since AG50 has been totally converted at 60 min. This figure shows negligible dye degradation in the absence of H_2O_2, whereas, high TOC removal is achieved by increasing H_2O_2 concentration in agreement with the apparent first-order-rate constant values (reported in the figure legend). The enhancement of dye mineralization with the H_2O_2 additions is because of the increased radical generation ($^{\bullet}OH$, $HO_2^{\bullet}$) by the catalytic decomposition of the hydrogen peroxide by the iron present in the Fe_2O_3–Al_2O_3 catalyst (Eqs. (4) and (5)). It has been accepted that the mechanism of hydrogen peroxide activation by iron ions in the homogeneous Fenton reaction is mainly through the generation of $^{\bullet}OH$ radicals [36,37]; however, it has also been proposed the formation of a highly reactive iron-oxo complex (ferryl ion, $Fe^{IV}O^{2+}$) as the oxidative intermediate in the homogeneous Fenton reaction [38,39]. Hence, a controversy exists whether the chemical mechanism involves radical production or ferryl ion generation as the active intermediate species. Nevertheless, in the heterogeneous Fenton reaction, the chemical pathway is less understood. It has been suggested either the adsorption of the H_2O_2 molecule onto $\equiv Fe^{III}$ sites or the adsorption of the organics [25,26]. However, the following steps have been proposed where the Fe^{3+} is reduced with the generation of less oxidative $HO_2^{\bullet}$ radicals, followed by Fe^{3+} regeneration with the formation of $^{\bullet}OH$ radicals.

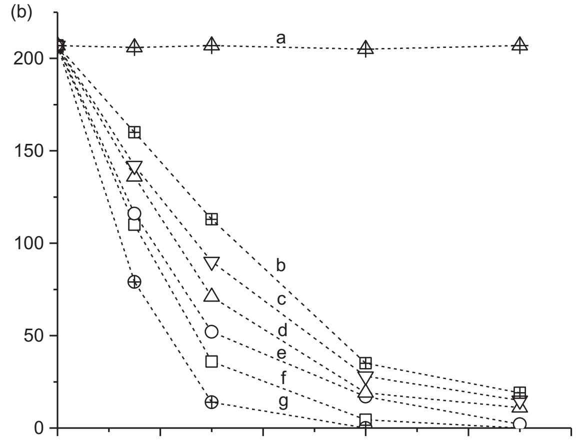


Fig. 2. TOC decrease as a function of hydrogen peroxide concentration. 0.82×10^{-3} mol L^{-1} AG50, initial TOC of 207 mg L^{-1}, pH 3, and 500 mg L^{-1} of Fe_2O_3–Al_2O_3 catalyst load calcined at 450°C. Concentration of H_2O_2 (mol L^{-1}): (a) 0, (b) 5×10^{-3} (0.028 min^{-1}), (c) 10×10^{-3} (0.031 min^{-1}), (d) 18×10^{-3} (0.035 min^{-1}), (e) 35×10^{-3} (0.042 min^{-1}), (f) 71×10^{-3} (0.064 min^{-1}), and (g) 71×10^{-3} (homogeneous, 0.090 min^{-1}).

$$X\text{–}Fe^{3+} + H_2O_2 \rightarrow X\text{–}Fe^{2+} + HO_2^{\bullet} + H^+ \tag{4}$$

$$X\text{–}Fe^{2+} + H_2O_2 \rightarrow X\text{–}Fe^{3+} + OH^- + OH^{\bullet} \tag{5}$$

where X represents the surface of the catalyst. It was also proposed [25] that the radicals can be generated in the surface of the solid so they are actually “caged” in the solid structure, subsequently reacting with the adsorbed reagents without radicals generation. Besides the indicated steps many other radical reactions can occur similar to those described in the homogeneous Fenton reaction [40].

Over 85% TOC reduction was achieved for all used H_2O_2 concentrations in AG50 degradation by heterogeneous Fenton reaction. These results clearly indicate that the H_2O_2 stoichiometry in the heterogeneous Fenton reaction does not correspond to that depicted in Eq. (3); such behavior is unlikely to be explained based on the oxidation states of nitrogen atom; thus, further research is required to clarify this phenomenon. The immobilized iron in the catalyst exhibits high catalytic effect since the usage of H_2O_2 can be reduced from its stoichiometry requirement and still high mineralization yields are efficiently achieved. Additionally, the heterogeneous Fenton catalyst can be easily removed and reused in several runs before the catalyst loses its catalytic effect.

The influence of calcination temperature on the heterogeneous catalyst is shown in Fig. 3. The temperatures used are 105°C (as dried), 300, 450, and 550°C. All used catalyst calcined temperatures show very good activity, since 99% TOC was removed using H_2O_2 stoichiometry. Additionally, TOC removal slightly decreased at H_2O_2 concentration higher than the stoichiometric value. This is explained by the hydroxyl radical scavenging effect of H_2O_2 when high concentrations are used. The $^{\cdot}OH$ radicals decompose H_2O_2 in water generating less oxidative $HO_2^{\cdot}$ radicals, according to Eq. (6),

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \tag{6}$$

It is also observed that high TOC reductions are achieved when ~half the concentration of H_2O_2 was used. Nevertheless, better control of iron content was achieved when the catalyst was subjected to thermal treatment, since 30% of iron leaching was observed for the catalyst dried at 105°C. Thermal treatment decreased iron leaching from the catalyst to less than 16% after 240 min of heterogeneous Fenton degradation.

3.2.2. Influence of solution pH

It is well known that $^{\cdot}OH$ radical generation is enhanced at $pH \leqslant 3$ in the homogeneous Fenton reaction and organic compounds are oxidized efficiently [14,40]. Nevertheless, at higher pH, iron ions participate in secondary reactions with hydroxide ions decreasing the $^{\cdot}OH$ radical generation; thus, the degradation efficiency is highly decreased or the degradation does not take place. However, having the Fe^{III} immobilized on the alumina support it was expected to obtain AG50 degradation at $pH > 3$, since iron-hydroxide compounds were less likely to form on the catalyst surface. Fig. 4 reports the profiles for TOC removal of AG50 during heterogeneous Fenton reaction at pH 3, 7, and 10. The degradation efficiency is highly enhanced at pH 3 as expected. However, higher pH values prevented the oxidation of this compound; similar results were reported on the heterogeneous Fenton oxidation of dye solutions using iron–alumina catalyst [23,24]. Muthuvel and Swaminathan reported that pH 3 was optimum for heterogeneous photo-Fenton degradation of Acid Violet 7 using Fe(III)–Al_2O_3 catalyst, and a sharp decoloration decrease was observed above this value [23]. Muthukumari et al. studied the photoassisted heterogeneous Fenton for the mineralization of azo dyes by Fe (II)–Al_2O_3 catalyst and also found that $pH > 3$, a decoloration detrimental effect was observed in both azo dye systems studied [24]. Thus, based on these studies, the alumina-based iron catalysts exhibit higher degradation efficiency in acidic pH.

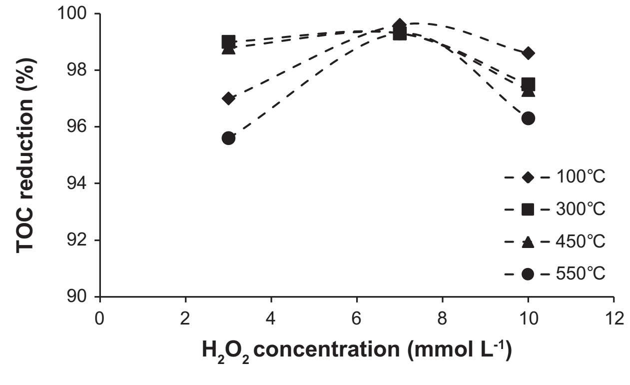


Fig. 3. TOC removal (initial TOC = 19.0 mg L^{-1}) vs. H_2O_2 concentration during the heterogeneous Fenton reaction for the degradation of 0.075×10^{-3} mol L^{-1} AG50 at pH 3, using 500 ppm catalyst calcined at different temperatures.

3.2.3. Influence of initial dye concentration

The initial dye concentration studied was between 0.75×10^{-3} and 10×10^{-3} mol L^{-1}; the amount of H_2O_2 used corresponded to the stoichiometry according to Eq. (3), while the amount of catalyst was kept constant. It is observed in Fig. 5 that over 98% TOC was removed in all cases indicating good catalytic activity of iron to activate H_2O_2. A decrease in TOC removal

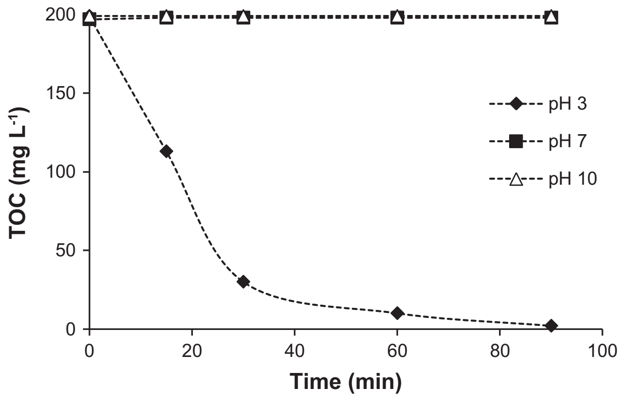


Fig. 4. TOC removal as a function of pH. 0.82×10^{-3} mol L^{-1} AG50, 500 ppm Fe_2O_3–Al_2O_3 catalyst calcined at 450°C and 71×10^{-3} mol L^{-1} H_2O_2.

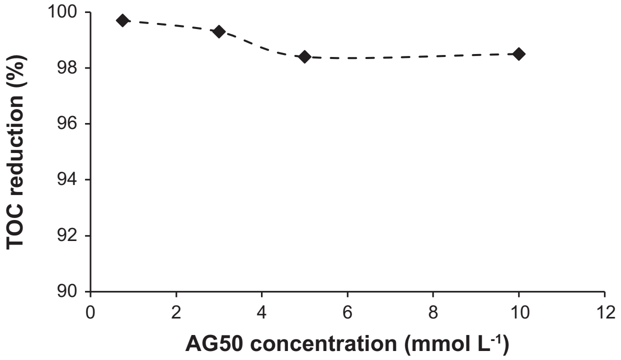


Fig. 5. TOC removal as a function of initial dye concentration at pH 3 with 500 ppm Fe_2O_3–Al_2O_3 calcined at 450°C. Initial TOC values (AG50 in mol L^{-1}): 190.2 (0.75×10^{-3}), 570.0 (3×10^{-3}), 950.0 (5×10^{-3}), 1900.0 (10×10^{-3}), stoichiometric H_2O_2 concentration was used according to the initial dye concentration.

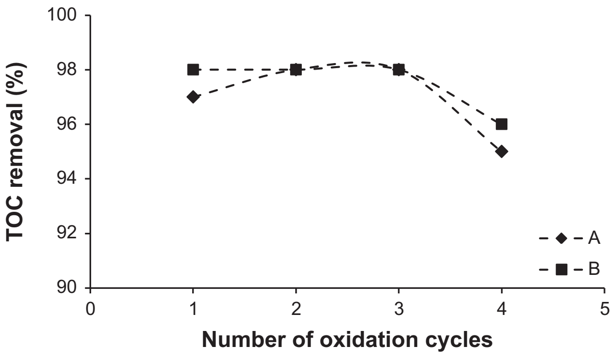


Fig. 6. TOC removal at 90 min of reaction vs. number of oxidation cycles from 1×10^{-3} mol L^{-1} AG50 solution containing 71×10^{-3} mol L^{-1} H_2O_2 at pH 3 with 500 ppm catalyst calcined at 450°C. Cycles **A**: addition of fresh dye solution and H_2O_2 to the used catalyst, **B**: addition of concentrated dye solution and H_2O_2 to the colorless treated solution to reuse the catalyst.

was also observed with increasing dye concentration. This can be explained on the basis that higher H_2O_2 doses are required to degrade higher dye concentrations; hence the high amount of H_2O_2 may react with $^{\bullet}OH$ radicals generating water and less oxidative $HO_2^{\bullet}$ radicals as stated in Eq. (6).

3.2.4. *Catalyst stability and reuse*

The stability of the catalyst was observed on the degradation of 100 mL of 1×10^{-3} mol L^{-1} AG50 using 500 ppm of catalyst load calcined at 450°C and 71×10^{-3} mol L^{-1} H_2O_2 in the heterogeneous Fenton reaction. Two types of experiments were carried out to assess the recyclability of the catalyst, and were carried out in the following manner: The experiments labeled with **A**, consisted on carefully removing the colorless solution from the reactor (to prevent catalyst loss) at 90 min of dye treatment to start a new AG50 discoloration by adding fresh solution of AG50 (at pH 3 and H_2O_2) to the used catalyst; whereas in the experiments labeled with **B**, the treated water in each cycle of 90 min of treatment was reused together with the used catalyst, and concentrated solutions of AG50 and H_2O_2 were added (adjusting the initial volume of the reactor and pH to start with same initial concentrations). TOC was measured at the beginning and end of each cycle. Fig. 6 shows that TOC removal efficiency decreases slightly after each cycle of catalyst reuse in both cases. This recycling study revealed that the catalytic activity was achieved at ~98% TOC removal for the first three runs and reduced to ~95% at the fourth run due to iron leaching or a possible alteration of the catalyst surface. The experiments conducted by reusing both the colorless treated water and the catalyst (experiments **B**) showed that the intermediate species produced during the dye degradation were completely degraded since the activity of the catalyst was not highly affected by surface modification with adsorption or accumulation of the intermediates on the catalyst surface. These experiments should have been conducted using more cycles to reuse the catalyst and observe the time in which the iron was exhausted from the catalyst due to leaching or a possible alteration of the surface of the catalyst. These results have shown that the active phase of the catalyst exhibits a very good activity during its reuse in four successive experiments while maintaining a high degree of mineralization of the textile AG50 dye after a total time of 6 h of catalyst reuse. The amount of iron lixiviated after the 6 h of successive catalyst reuse is 5.5 mg L^{-1}. Based on these results, it can be inferred that all the iron would be lixiviated after using the catalyst ~15 times consecutively or ~22 h (considering each cycle lasts 90 min).

4. Conclusions

This study shows that the ferric ions loaded on the surface of neutral $Al(OH)_4^-$ gel and then calcined at different temperatures, obtaining Fe_2O_3–Al_2O_3, is an efficient catalyst in the heterogeneous Fenton reaction for the mineralization of aqueous AG50. The thermal treatment gives long-term stability to the Fe_2O_3–Al_2O_3 catalyst because it minimizes iron leaching from the catalyst. Thus the Fe_2O_3–Al_2O_3 catalyst is highly efficient for the degradation of AG50 after being used in several cycles during the dye treatment. It was found that AG50 degradation increased by increasing the hydrogen peroxide concentration, but it decreased by increasing the dye concentration in the heterogeneous Fenton process. The Fe_2O_3–Al_2O_3 catalyst is highly efficient in the heterogeneous Fenton process for the reduction of initial high TOC contents in aqueous solution. The kinetic study indicated that the mineralization kinetics of AG50 followed the first-order kinetic.

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