Fe(III)-catalyzed degradation of persistent textile dyes by chlorine at slightly acidic conditions: the crucial role of $\text{Cl}_2^{\bullet-}$ radical in the degradation process and impacts of mineral and organic competitors

Fatima Zohra Meghlaoui ^a, Slimane Merouani ^a, Oualid Hamdaoui ^{b*}, Abdulaziz Alghyamah ^b, Mohammed Bouhelassa ^a, Muthupandian Ashokkumar ^c

^a Laboratory of Environmental Process Engineering, Faculty of Process Engineering, University Salah Boubnider – Constantine 3, P.O. Box 72, 25000 Constantine, Algeria

^b Chemical Engineering Department, College of Engineering, King Saud University, P.O. Box 800, 11421 Riyadh, Saudi Arabia

^c Department of Chemistry, The University of Melbourne, Parkville, Victoria 3010, Australia

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: [10.1002/apj.2553](https://doi.org/10.1002/apj.2553)

* The corresponding author (O. Hamdaoui)

E-mail address: ohamdaoui@ksu.edu.sa

Abstract

In this work, we have explored for the first time the potential application of trace-Fe(III)/chlorine system as an innovative oxidation technology for the degradation of persistent textile dyes. Fe(III)/chlorine combination improved the dye removal by ~ 40% within 30 s, as compared with chlorination alone, mainly through a radical pathway induced by the catalytic activation of chlorine in the presence of Fe(III). A chemical probe method was used for identifying the main reactive species. $\text{Cl}_2^{\bullet-}$ was found to be the key species responsible of huge abatement of dyes in the Fe(III)/chlorine system, whereas $^{\bullet}\text{OH}$ and $\text{Cl}^{\bullet}$ can participate with only ~ 5% in the overall removal efficiency. At pH 3, 77% of reactive green 12 (RG12) was removed after 30 s, and then the removal efficiency diminished to 60% at pH 4, 20% at pH 5 and ~ 10% at pH 6 and 7. However, the best implication of free radicals was achieved at pH 4, at which the degradation rate was 3.3 times higher than that of chlorination alone. The dye removal efficiency increased with an increase in chlorine and iron loads up to certain optimums (~50 μM of iron and ~ 250 μM of chlorine), but detrimental effect was observed at higher dosage levels. An increase in the solution temperature notably accelerated the removal yield (i.e. 81% of RG12 was removed at 50 °C against 67% at 30 °C and 57% at 10 °C). NO_2^- and HSO_3^- as well as the cationic surfactant Adogen 464 showed strongest inhibiting effect on the performance of the process. Based on these findings, the Fe(III)/chlorine process is highly efficient in removing dyes from wastewaters.

Keywords: Fe(III)/chlorine process; Innovative oxidation technology; Textile dyes; Degradation; $\text{Cl}_2^{\bullet-}$ radical; Mineral anions

1. Introduction

Dyes are one of the most hazardous chemical compound classes found in industrial effluents and need to be treated since their presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora^{1,2}. They are also aesthetically objectionable for drinking and other purposes and can cause dermatitis, allergy, skin irritation and also provoke cancer and mutation in humans.^{1,3,4}

Advanced oxidation processes (AOPs) which involve the generation of highly reactive and non-selective hydroxyl radical ($\bullet\text{OH}$, $E^0 = 2.8 \text{ V}$) are of interest for the destruction of persistent and non-biodegradable organic pollutants in wastewater.⁵ Among these techniques, Fenton's ($\text{Fe(II)}/\text{H}_2\text{O}_2$) and Fenton-like ($\text{Fe(III)}/\text{H}_2\text{O}_2$) reagents have been the subject of extensive studies in order to examine the efficiency of the process for the removal of organic pollutants^{6,7}. In Fenton process, $\bullet\text{OH}$ is produced from the direct catalytic action of iron(II) on H_2O_2 as in Eq. 1. The Fenton process can be efficiently applied when the pH optimum value of the polluted aqueous medium is about 2.8–3.0.^{7,8} Indeed, in these conditions, the Fenton's reaction can be propagated by the catalytic behavior of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple, in which Fe^{2+} ion is regenerated from the so-called Fenton-like reaction between Fe^{3+} and H_2O_2 as well as Fe^{3+} and $\text{HO}_2\bullet$ radical (Eqs. 2 and 3)^{6,9}. It has been reported that the Fenton-like reaction (3) is much slower than the Fenton's reaction itself (Eq. 1)¹⁰

However, all Fenton-based process have several operating limitations such as (i) iron precipitation as $\text{Fe}(\text{OH})_3$ at $\text{pH} > 3$, (ii) the use of relatively high dosages of iron and H_2O_2 and (iii) the high cost of H_2O_2 and its facile thermal decomposition at room temperature.⁹ Nowadays, the substitution of H_2O_2 by NaClO in Fenton process has become an interesting task due to (i) the very low cost and the marked stability of NaClO , (ii) the very fast reaction between $\text{Fe}(\text{II})$ and chlorine ($k \sim 10^4 \text{ M}^{-1} \text{ s}^{-1}$), which is suspected to generate strong reactive species and (iii) the use of very low concentration of reagents.^{11,12} Behin et al.¹² have reported that sodium hypochlorite may be an alternative to hydrogen peroxide in Fenton process. The degradation of simulated petroleum wastewater was performed by Fenton and $\text{Fe}(\text{II})/\text{NaClO}$ at various oxidants and iron loads for $\text{pH} \leq 4$.¹² Their results showed strong similarities between the two processes, but higher oxidation efficiency was obtained with Fenton system. Kaluzna-Czaplinska et al.¹³ have compared the efficiency of chlorine with $\text{Fe}(\text{II})/\text{chlorine}$ at $\text{pH} 3.5$ by varying iron load in the range of 5-30 mg/L and keeping NaClO at 0.5 mg NaClO per mg of Acid Brown 349. It was found that efficient COD removal was obtained by the combined process. More recently, our research group has studied in detail the effect of $\text{Fe}(\text{II})/\text{chlorine}$ process on the degradation of several textile dyes under various experimental conditions. A drastic acceleration in the degradation rate of all dyes was obtained.¹¹

The underlying reactions mechanism for the $\text{Fe}(\text{II})/\text{chlorine}$ system is until now under debate. Candeias¹⁴ showed that hydroxyl radical was implicated in the system with 27%, as predicted from the hydroxylation of benzoate. The other portion was attributed to non-determined reactive species. $\bullet\text{OH}$ radical was also determined recently in the sludge conditioned with $\text{Fe}(\text{II})/\text{Ca}(\text{ClO})_2$. In contrast, Folkes et al.¹⁵ reported that the reaction of

iron(II) with HClO yielded reactive intermediates distinguishable from hydroxyl radicals (i.e., presumably, chlorinated reactive species (CRS)). In our recent study,¹¹ based on thermodynamic analysis, a chain reaction mechanism was proposed for the Fe(II)/chlorine system and the reactive species involved in this system were identified using specific radical scavengers. It was found that $\text{Cl}_2^{\bullet-}$ radical plays the dominant role in the oxidative event of Fe(II)/chlorine system, although other reactive radicals such as $\bullet\text{OH}$, $\text{Cl}^\bullet$ and $\text{ClO}^\bullet$ may have also contributed to the degradation process.

In the present work, a new approach based on combining chlorine with Fe(III) rather than Fe(II) has been explored for the first time. The degradation of several textile dyes by the Fe(III)/chlorine was investigated at various experimental conditions. A reaction mechanism has been proposed and the main radical species responsible for the oxidation are identified. Additionally, the impact of several organic and mineral additives was assessed to evaluate the process efficacy if the process was to be applied in treating real textile effluents.

2. Experimental section

2.1. Reagents

All solutions were prepared using reagent-grade chemicals and deionized water. Basic fuchsin (abbreviation: BF; CAS number: 569-61-9; molecular formula: $\text{C}_{20}\text{H}_{20}\text{ClN}_3$, molecular weight: $337.84 \text{ g mol}^{-1}$), toluidine blue (abbreviation: TB; CAS number: 6586-04-5, molecular formula: $\text{C}_{15}\text{H}_{16}\text{ClN}_3\text{S} \cdot 0.5\text{ZnCl}_2$, molecular weight: $373.97 \text{ g mol}^{-1}$), chlorazol black (abbreviation: CB, molecular formula: $\text{C}_{34}\text{H}_{25}\text{N}_9\text{Na}_2\text{O}_7\text{S}_2$), C.I. reactive green 12 (abbreviation: RG12; CAS number: 12225-80-8; molecular formula: $\text{C}_{60}\text{H}_{29}\text{Cl}_3\text{N}_{16}\text{NiO}_{21}\text{S}_7 \cdot \text{H}_2\text{O}$, molecular weight: $1837.7 \text{ g mol}^{-1}$) and sodium hypochlorite

(NaOCl) solution (available chlorine ~15%) were purchased from Sigma-Aldrich. All other reagents (t-butanol, sodium azide, benzoic acid, phenol, nitrobenzene, ferric sulfate, sulfate ferrous, sodium hydroxide, sulfuric acid, sodium chloride, sodium sulfate, sodium nitrite, sodium nitrate, potassium bromide, sodium sulfite, surfactants and humic acid) were also supplied by Sigma-Aldrich and used as received.

2.2. Experimental procedure

Experiments were performed under magnetic stirring in a cylindrical water-jacketed glass reactor (capacity: 300 mL, $\phi_{\text{int}} = 6$ cm) to control the solution temperature through circulating water, i.e. provided from a RC6 Lauda thermo-cryostat, in the cell-jacket at controlled flux. Stock solutions of dyes (1 g/L, pH 5), chlorine (10 mM, pH 5) and iron (5 mM, pH 3) were prepared using deionized water and preserved in the dark at 5 °C. Oxidative trials were conducted using a 200 mL of air-equilibrated solutions (the reactor was open to air). For each experiment, the solution of dye and iron was firstly prepared at desired concentrations, pH and temperature. After that, chlorine was added and the chronometer was turned on, this was the time zero for the reaction. Samples aliquots (3 mL) were withdrawn at different time interval using a glass syringe and transferred to a quartz cell (1 cm optical path length) of a UV-vis. spectrophotometer (Jenway 6405) to measure the absorbance of dyes at their maximum absorption wavelengths (region ($\lambda_{\text{max, RG12}} = 614$ nm, $\lambda_{\text{max, TB}} = 628$ nm, $\lambda_{\text{max, CB}} = 578$ nm, $\lambda_{\text{max, BF}} = 543$ nm)). Calibration curves, established based on Lambert-Beer law, were used for determining the concentration of dyes during the oxidation runs. The solution pH was adjusted using NaOH or H₂SO₄ and displayed by a Jenway 3505 pH-meter. All experiments were repeated at least three times and data were reported as averages.

3. Results and discussion

3.1. Efficiency of the Fe(III)/chlorine process

Fig. 1(a) shows the effect of Fe(III) concentration in the range of 0-100 μM on the removal kinetics of RG12 (30 mg/L) in the presence of 250 μM of chlorine at pH 4 and temperature of 20 $^{\circ}\text{C}$. As clearly seen, the dye removal efficiency increased significantly with increasing Fe(III) from 15 to 50 mM, after which a further increase in iron concentration did not show notable change in the RG12 removal. In the absence of iron, chlorine eliminated 19% of RG12 within 30 s; the removal efficiency increased to 30%, 42% and 60% when Fe(III) was present at 15, 25 and 50 μM , respectively. After 5 min, Fe(III)/chlorine process eliminated 80% of RG12 against 56% for chlorine alone. The removed amount of the dye upon chlorine and Fe(III)/chlorine processes as well as the resulted enhancement index (EI) are shown in Fig. 2(b) for different iron doses. The EI is defined as the ratio of RG12 removal by Fe(III)/chlorine process to that of chlorination alone (both evaluated after 30 s of reaction). The EI increased from 1.6 for 15 μM of Fe(III) to 2.2 for 25 μM , 3.3 for 50 μM and 3.5 for 100 μM . The viability of the Fe(III)/chlorine process was not only limited to the RG12 dye degradation but similar efficient removal rates were obtained for toluidine blue (TB), chlorazol black (CB) and Basic fuchsin (FB), as can be seen in Fig. 2. Significant enhancement indexes of 5, 3.66 and 2.4 were obtained for TB, CB and BF, respectively. All these improvements by the Fe(III)/chlorine system was mainly attributed to the formation of reactive species generated by the catalytic activation of chlorine. It should be noted that the iron doses used in this study were much lower than those used in the Fenton-like reaction.

3.2. Proposed mechanism for Fe(III)/chlorine system

We have recently demonstrated that the Fe(II)/chlorine process yields huge enhancements in the degradation of several synthetic dyes, as compared with chlorination alone.¹¹ It was confirmed through radicals probing technique that some reactive species such as $\bullet\text{OH}$ and other chlorinated reactive species ($\text{Cl}\bullet$, $\text{ClO}\bullet$ and $\text{Cl}_2\bullet^-$) may be formed *via* direct catalytic action of iron(II) on chlorine.¹¹ A reaction mechanism consisting on 19 reactions involving initiation, propagation and termination steps has been proposed for the system Fe(II)/chlorine.¹¹ To explain the obtained results for the case of Fe(III)/chlorine system, the earlier mechanism has been partially modified by including the initial reactions required for the generation of Fe(II), like in the Fenton-like process.^{6,8} The first step consists on the reduction of Fe(III) into Fe(II) by chlorine as in Eq. (4). Then the process described previously (Ref. 11) will be triggered. The overall reaction scheme is shown in Table 1.

Eq. 4 has been proposed by complete analogous to the Fenton-like reaction (Eq. 2) in which Fe(III) was firstly reduced into Fe(II) by H_2O_2 . Thermodynamically, both H_2O_2 and HClO are strong oxidants of comparable oxidation potentials (1.77 V for and 1.49 for HClO)¹⁶. The Fenton-like reaction has been completely accepted with the chemistry community even through H_2O_2 and Fe(III) exists also at higher oxidation state exactly like our case (HClO and Fe(III)). In the Fenton-like system, Eq. 2 acts only as precursor of Fenton system ($\text{Fe(II)}/\text{H}_2\text{O}_2$). Correspondingly, Eq. 4 proposed for the system Fe(III)/ HClO may also act as precursor of the system Fe(II)/chlorine, which has proven their high efficiency in degrading organic pollutants via radical pathway involving $\bullet\text{OH}$, $\text{ClO}\bullet$ and $\text{Cl}_2\bullet^-$ radicals.¹¹

According to the proposed mechanism, the efficiency of Fe(III)/chlorine process should be lower than that of Fe(II)/chlorine as a part of chlorine will initially be used to generate Fe(II), which is one of the precursor of the Fe(II)/chlorine system. This speculation was tested by conducting RG12 degradation experiment by Fe(II)/chlorine in the same conditions as that of Fe(III)/chlorine process (Fig. 3). From Fig. 3, it is seen that 87% of RG12 was removed by Fe(II)/chlorine at the first 30 s, instead 60% for the case of Fe(III)/chlorine. The loss in the removal efficiency by Fe(III)/process (~ 27%) can be associated to the contribution of reaction (4) in the overall consumption of chlorine to yield Fe(II).

3.3. Probing of reactive species

Efforts were made to identify the involvement and contribution of different reactive species derived from the Fe(III)/chlorine reaction in the oxidation of RG12. According to the mechanism shown in Table 1, several radical species, *i.e.*, principally $\bullet\text{OH}$, $\text{Cl}\bullet$, $\text{ClO}\bullet$ and $\text{Cl}_2\bullet^-$ may be created in the Fe(III)/chlorine system. These species are the most expected oxidants as they have higher redox potentials (2.43 V for $\text{Cl}\bullet$, 2.13 V for $\text{Cl}_2\bullet^-$ and 1.5-1.8 V for $\text{ClO}\bullet$) and are mostly implicated in the photoactivated chlorine process.^{17,18} Additionally, these radicals react with organic matters practically with the same mechanisms (H-atom abstraction, electron transfer or addition to unsaturated bands).¹⁸ The second-order rate constants for reactions involving these radicals varies in the order $\sim 10^8$ - $10^{10} \text{ M}^{-1}\text{s}^{-1}$ for $\bullet\text{OH}$ and $\text{Cl}\bullet$, $\sim 10^7$ - $10^9 \text{ M}^{-1}\text{s}^{-1}$ for $\text{ClO}\bullet$ and 10^2 - $10^6 \text{ M}^{-1}\text{s}^{-1}$ for $\text{Cl}_2\bullet^-$.^{17,18}

The contribution of the above radicals as well as direct chlorination in the degradation of RG12 by the Fe(III)/chlorine was evaluated using the following scavengers: nitrobenzene

(NB), benzoic acid (BA), t-butanol (TBA), phenol (Ph), sodium azide (NaN_3) and ascorbic acid (AscA). Table 2 shows the reactivity of NB, BA, Ph, N_3^- and TBA with $\bullet\text{OH}$, $\text{Cl}\bullet$, $\text{ClO}\bullet$ and $\text{Cl}_2^{\bullet-}$. Traditionally, ascorbic acid as a classical reducing agent was mostly used as a common scavenger for both free radicals and chlorine.^{19–21} It has been used to confirming the contribution of both free radicals and chlorine in the degradation process. N_3^- and phenol can rapidly scavenge all radicals. Therefore, they were used for approximating the contribution of direct chlorination in the Fe(II)/chlorine oxidative process. NB only reacts with $\bullet\text{OH}$ and it is resistance to CRS and chlorine.²² Hence, NB was used as radical selective probe to differentiate the role of $\bullet\text{OH}$ and CRS+chlorine. BA can scavenge $\bullet\text{OH}$ and $\text{Cl}\bullet$ but its scavenging effect on $\text{ClO}\bullet$, $\text{Cl}_2^{\bullet-}$ and chlorine is negligible. It has been then used to determine indirectly the contribution of $\text{Cl}\bullet$. TBA can scavenge $\bullet\text{OH}$, $\text{Cl}\bullet$ and $\text{ClO}\bullet$ and its scavenging effect on $\text{Cl}_2^{\bullet-}$ is negligible. TBA was used for appreciating the plausible role of $\text{Cl}_2^{\bullet-}$.

The effect of all above scavengers on the removal kinetics of RG12 is shown in Fig. 4. The used initial concentrations of NB, BA, Ph, AscA and NaN_3 were 10 mM, but that of TBA was 100 mM. These high concentrations were selected to ensure that radical scavengers are in excess in the solution. It is clearly observed from Fig. 4 that ascorbic acid suppressed 98% of the dye removal, indicating that both reactive radicals and molecular chlorine were involved in the degradation process. Azide ions and phenol diminished the removal efficient by ~ 95% and 98%, meaning that direct chlorination of RG12 contributed only ~ 5 to 8% to the degradation efficiency of the dye upon Fe(III)/chlorine treatment. The addition of NB as a selective quencher of $\bullet\text{OH}$ reduced the RG12 removal from 60% to 55%. Thus, $\bullet\text{OH}$ contributes by only ~ 5% in the overall removal rate of RG12 by Fe(III)/chlorine process.

Besides, BA which quenches both $\bullet\text{OH}$ and $\text{Cl}\bullet$ resulted in only 12% reduction in the dye removal, indicating that $\text{Cl}\bullet$ contributes about 7% (because $\bullet\text{OH}$ sole contributed by 5 %). Therefore, $\text{Cl}_2^{\bullet-} + \text{ClO}\bullet$ may have contributed the major part ($\sim 80\%$) to the overall effect of Fe(III)/chlorine system. However, given that TBA, which could quench all radicals except $\text{Cl}_2^{\bullet-}$, shows a similar influence as that of BA ($\sim 10\%$ reduction, as compared with the non-quenched system), it could be concluded that $\text{ClO}\bullet$ has an insignificant role whereas $\text{Cl}_2^{\bullet-}$ could be the dominant reactive species in the degradation of the dye by the system Fe(III)/chlorine. This conclusion is quantitatively in agreement with that obtained for the system Fe(II)/chlorine.¹¹

Based on this analysis, the detrimental effect of high Fe(III) dosage (Fig. 1) may only be due to the quenching of $\text{Cl}_2^{\bullet-}$ radical by the excess of iron as given in the following reaction:

3.4. Effect of chlorine dosage

Different amounts of chlorine were used to investigate the effect of chlorine dosage on RG12 oxidation at pH 4 and $[\text{Fe(III)}]_0 = 50 \mu\text{M}$. The results presented in Fig. 5(a), indicate that RG12 oxidation increases with an increase in chlorine concentration up to $1000 \mu\text{M}$ for the case of Fe(II)/chlorine system¹¹. Eliminations of 37%, 45%, 60% and 73% were recorded for 25, 100, 250 and $1000 \mu\text{M}$ of chlorine. As shown in Table 1, the concentration of free radical might have increased with an increase in chlorine concentration, which improved the degradation rate of the dye. However, the generated radicals can be scavenged by chlorine itself when it is used at much higher concentration.¹¹ This case was not observed in this study,

probably because the highest chlorine dose used herein (1000 μM) did not reach the critical level to slow down the degradation process. Candeias et al.¹⁴ have studied the reaction between ferrocyanide, as source of Fe(II), and chlorine at pH 7. They found that the rate of ferrocyanide decomposition increased linearly with increasing chlorine dosage up to 1000 μM . Similarly, no detrimental effect of high chlorine dose was observed by Kong et al.²⁴, Fang et al.²⁵ and Qin et al.²⁶ who investigated the degradation of several organic contaminants by UV/chlorine process.

Importantly, the beneficial effect of Fe(III)/chlorine, as compared to chlorination alone, increased with an increase in $[\text{chlorine}]_0$ in the range 25-250 μM , as can be seen in Fig. 5(b). After 30 s of reaction, chlorine alone at 25 μM eliminated 1 mg/L of RG12, but in the presence of iron the removal increased to 11 mg/L. At 250 μM , the combined process removed 19 mg/L of RG12 against 5.7 mg/L for chlorination alone. However, the enhancement index showed the best value, 10.57, at 25 μM of chlorine and then decreased to 6 at 100 μM , 3.5 at 25 μM and 2.2 at 1000 μM .

3.5. Effect of pH

In iron-based treatment techniques of wastewater, the pH is probably one of the most important and crucial parameters that should always be taken into consideration. In our case, the process sensitivity to the initial solution pH was investigated at Fe(III) and chlorine dosages of 50 μM and 250 μM , respectively. The concentration of RG12 was kept at 30 mg/L. The obtained results are presented in Fig. 6(a) whereas Fig 6(b) show the amount of dye removed after 30 s by chlorination and Fe(III)/chlorine process as well as the resulted enhancement index. As can be seen, the solution pH affected strongly the RG12 degradation

by Fe(III)/chlorine. The degradation rate decreased markedly with pH rise in the range 3-7. At pH 3, 77% of RG12 was removed after 30 s, and then the removal efficiency diminished to 60% at pH 4, 20% at pH 5 and ~ 10% at pH 6 and 7. Correspondingly, chlorine alone eliminated 53% of RG12 at pH 3, 19% at pH 4 and ~ 10% for pH > 4 (Fig. 5(b)). The enhancement index varies as 1.44 at pH 3, 3.3 at pH 4, 2.4 at pH 5 and practically ~1 for pH > 5.

The solution pH affects both iron(III) and chlorine speciations. The pKa values of chlorine are ~ 1 and 7.6.¹⁸ Chlorine species are predominately distributed as: Cl₂ at pH < 3, hypochlorous acid (HClO) at 4 < pH < 6.5 and hypochlorite (ClO⁻) at pH ≥ 8.¹⁸ The chemical activity of chlorine species decreases in the order Cl₂ < HClO < ClO⁻.²⁷ Additionally, the reactivity of HClO with organics is much higher at slightly acidic condition, *i.e.*, pH 4, than that at near neutral pHs (5–6).²⁷ On the other hand, the speciation diagram of Fe(III) indicated that Fe³⁺ ions is predominated for pH < 2, Fe(OH)²⁺ predominated at pH 4 and Fe(OH)₂⁺ predominated at pH 4-6.^{8,28} However, the Fe(III) precipitates as Fe(OH)₃ at pH 6, and at pH 7, the fraction of Fe(OH)₃ is about 10%.^{8,28} The best efficacy of the Fenton-like process (Fe(III)/H₂O₂) was observed at ~ pH 3 when Fe(OH)²⁺ is the predominant species. Sanz et al.²⁸ have reported that in Fenton-like system the Fe(OH)²⁺ is responsible for the generation of hydroxyl radicals process and not the Fe³⁺ itself.

Based on these specification, the effect of pH on the degradation of RG12 by Fe(III)/chlorine process can be explained as follow: the higher degradation at pH 3 is due to a combination of direct chlorination and free radical reaction. It has been estimated that chlorination contributed in the Fe(II)/chlorine by 37% rather than < 10% for pH > 3.¹¹

Additionally, ~2% of Cl_2 exists at pH 3. This species is much active than other chlorine species and makes the reaction faster even at very low concentrations.²⁷ At pH 4, chlorine retained the form HClO but Fe(III) exists as a mixture of Fe(OH)^{2+} (25%) and Fe(OH)_2^+ (75%). The degradation rate of dye decreased by 17% compared to that at pH 3, revealing that, as in Fenton- like system, Fe(OH)^{2+} is more reactive with HClO than Fe(OH)_2^+ . Therefore, an increase in the fraction of Fe(OH)_2^+ with an increase in pH to 5 and 6 is likely the reason of the continuous drop in RG12 removal efficacy at these pH levels. At pH 7, chlorine exists as a mixture of HClO (80%) and ClO^- (20%). Thus, in addition to the reasons of pH 5 and 6, 10% of iron is as Fe(OH)_3 and all Fe(II) species is unreactive with ClO^- . Consequently, it is recommended that the Fe(III) /chlorine process should be applied at pH 4 to avoid (i) strong acidification (as at pH 3), (ii) lower degradation performance (i.e. for pH > 4), and (iii) sludge formation during the treatment.

3.6. Effect of liquid temperature

The effect of solution temperature on the efficiency of RG12 removal by chlorine and Fe(III) /chlorine process was investigated for 50 μM of Fe(III) and 250 μM of chlorine and the obtained results are summarized in Fig. 7. This data clearly shows that higher temperatures favor higher removal rate of the dye by the combined system. 81% of RG12 was removed at 50 °C against 67% at 30 °C and 57% at 10 °C. Additionally, the removed efficiency increased linearly with temperature rise for both chlorination and Fe(III) /chlorine process, as indicated in Fig. 7(b). However, the ratio between the removal with Fe(III) /chlorine to that with chlorine alone decreased from 6.34 at 10 °C to 3.3 at 20 °C and then to 1.81 at 50 °C. This is due to the fact that the slope of the removal rate of the dye with chlorination alone is greater

than that obtained by Fe(III)/chlorine system, as showed the data of Fig. 7(b). Nevertheless, higher level of elimination were always obtained with Fe(III)/chlorine process.

3.7. Effect initial dye concentration

RG12 degradation study by chlorine and Fe(III)/chlorine was carried out at concentration range of 10-100 mg/L, keeping other parameters constant ($[\text{Fe(III)}]_0 = 50 \mu\text{M}$, $[\text{chlorine}]_0 = 250 \mu\text{M}$ and pH 4). It can be seen from Fig. 8(a) that the initial concentration of the pollutant and the removal efficiency are inversely related. Removals of 68%, 63 % and 30% was reached for $C_0 = 10, 30$ and 100 mg/L , respectively. On the other hand, the removed amount at 30 s augmented significantly from 7 mg/L for $C_0 = 10 \text{ mg/L}$ to 19 and 32 mg/L for, respectively, $C_0 = 30$ and 100 mg/L (Fig. 8(b)), indicating higher degradation rate at higher initial dye concentration. All these observations are exactly similar to those reported by Meghlaoui et al.¹¹ for the degradation of RG12 by Fe(II)/chlorine system. In general, at fixed dosage of Fe(III) and chlorine, the generation rate of free radicals is constant. Increasing C_0 in the reacting medium results in limiting the radical-radical recombination and overleaping the radicals-dye reaction. Thus, higher conversion rates would be associated to higher C_0 .²⁹ It can also be observed from Fig. 8(b) that the enhancement index increased with an increase in C_0 up to $\sim 30 \text{ mg/L}$ and declined beyond this concentration. Therefore, the best useful effect of the Fe(III)/chlorine system was obtained at moderate concentration of pollutants.

3.8. Effect of mineral salts

As inorganic ions constitute a major part of the water matrix, the degradation of RG12 by Fe(III)/chlorine system was accomplished in selected aqueous electrolyte solutions. The effect of different salts (NaCl , Na_2SO_4 , NaNO_2 , NaNO_3 , KBr and Na_2SO_3) was studied at pH

4 by adding each salt at 1, 10 and 50 mM under constant dosages of iron (50 μM) and chlorine (250 μM) (Fig. 9). As can be seen Cl^- , SO_4^{2-} , NO_3^- and Br^- have no influence at 1 mM while nitrite and sulfite drastically inhibited the degradation of the dye (RG12 removal was suppressed at 83% for sulfite and 95% for nitrite). In fact, among the above anions, HSO_3^- and NO_2^- have shown a strong reactivity toward $\text{Cl}_2^{\bullet-}$ radical (Eqs. 23 and 24).²³

Above 1 mM, chloride enhanced the degradation of the dye mainly through increasing the concentration of $\text{Cl}_2^{\bullet-}$ (Eq. 6). This is another confirmation of the responsibility of this radical in the degradation of RG12 in the Fe(III)/chlorine system. For SO_4^{2-} , NO_3^- and Br^- , their partial inhibiting effects (*i.e.* 20% inhibition max.) was observed only at higher concentration (50 mM); the concentration at which sulfite and nitrite completely suppress the degradation of the dye.

3.9. Effect of organic competitors

The effect of humic acids (HA: 5-20 mg/L) as natural organic matter and four surfactants (SDS, Tween 20, Tween 80 and Adogen 464) on the degradation of RG12 by Fe(III)/chlorine was investigated at pH 4 by fixing iron and chlorine concentration at 50 and 250 μM , respectively (Fig. 10). The surfactants concentrations were selected to be lower than their critical micelle concentration (CMC). HA reduced the RG12 removal by 26% at 1 mg/L and 42% at 20 mg/L, showing a significant retarding in the degradation rate. On the other hand, non-ionic and anionic surfactants (triton X-100 and SDS, respectively) did not show significant reduction in the degradation rate of the dye (at max. 15% reduction was recorded)

whereas adogen 464 (cationic surfactant) decreases significantly the treatment yield by 24% at 1 μM and 72% at 100 μM . It seems that the reactivity of $\text{Cl}_2^{\bullet-}$ is strongly affected by the charge of surfactants. In fact, this radical is very selective for olefins and aromatics containing hydroxyl or amino groups.²²

4. Conclusion

The system Fe(III)/chlorine could produce reactive species capable of degrading textile dye at much higher rates than the chlorine alone. The principal advantages of this developed process are that is very easy to manipulate, not expensive, highly efficient in removing dyes and may be operated at pH relatively higher than that of Fenton-like system. The process is strongly sensitive to operational conditions. Optimum concentrations of chlorine and iron(III) have been obtained for the best performance of the process. Operating at higher temperature generated higher concentration of reactive species which accelerated markedly the degradation of pollutants. Analysis of the process efficacy in the presence of several mineral anions and organic additives indicated that some anions, i.e., nitrite and sulfite, and surfactants, i.e. adogen 464, drastically suppressed the chemical activity of the Fe(III)/chlorine process toward the degradation of pollutants. Beside, based on using some specific radical scavengers, the species involved in the degradation system were found to be mainly $\text{Cl}_2^{\bullet-}$ radical. This radical is very selective and have longer lifetime than all other radicals formed in the system. Based on their properties, $\text{Cl}_2^{\bullet-}$ reacts efficiently with textile dyes inducing higher removal rates. However, further analysis such as the identification of the degradation by-products is still necessary for the process viability. This task, together with the COD, TOC and toxicity analysis, will be conducted in the future.

We would like to notice that the initial objective of the present study was not to deepen into the reaction mechanism between Fe(III) and HClO and process cost, but to show for the first time that the system Fe(III)/chlorine has a potential application in the degradation of persistent organic dyes in aqueous media. Nevertheless, the reaction mechanism merits further deepening studies that will be conducted together with the economic analysis of the process (including process-cost comparison with Fe(II)/chlorine and Fe(III)/H₂O₂) in the near future.

Acknowledgments

The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding this work through research group No. RG-1441-501.

References

1. Bazrafshan E, Mostafapour FK, Hosseini AR, Raksh Khorshid A, Mahvi AH. Decolorisation of reactive red 120 dye by using single-walled carbon nanotubes in aqueous solutions. *Journal of Chemistry*. 2013;Article ID:1–8.
2. Bazrafshan E, Alipour MR, Mahvi AH. Textile wastewater treatment by application of combined chemical coagulation, electrocoagulation, and adsorption processes. *Desalination and Water Treatment*. 2016;57(20):9203–9215.
3. Mirzadeh SS, Khezri SM, Rezaei S, Forootanfar H, Mahvi AH, Faramarzi MA. Decolorization of two synthetic dyes using the purified laccase of *Paraconiothyrium* variable immobilized on porous silica beads. *Journal of Environmental Health Science and Engineering*. 2014;12(1):1–9.
4. Dalvand A, Nabizadeh R, Reza Ganjali M, Khoobi M, Nazmara S, Hossein Mahvi A. Modeling of Reactive Blue 19 azo dye removal from colored textile wastewater using L-arginine-functionalized Fe₃O₄ nanoparticles: Optimization, reusability, kinetic and equilibrium studies. *Journal of Magnetism and Magnetic Materials*. 2016;404:179–189.
5. Stefan MI. *Advanced oxidation processes for water treatment: Fundamentals and applications*. London, UK: IWA Publishing; 2017.
6. Sillanpaa M, Ncibi MC, Matilainen A. Advanced oxidation processes for the removal of natural organic matter from drinking water sources: A comprehensive review. *Journal of Environmental Management*. 2018;208:56–76.
7. Fdil F, Aaron J, Oturan N, Chaouch A, Mehmet A. Dégradation photochimique des

- herbicides phénoxyalcanoïques en milieux aqueux aqueous media. :304–311.
8. Pignatello JJ, Oliveros E, MacKay A. Advanced oxidation processes for organic contaminant destruction based on the fenton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology*. 2006;36(1):1–84.
 9. Vasquez-Medrano R, DorianPratoGarcia, Vedrenne M. Ferrioxalate-mediated processes. In: Ameta SC, Ameta R, eds. *Advanced oxidation processes for waste water treatment - Emerging green chemical technology*. London, UK: Academic press; 2018:89–113.
 10. Brillas E, Sirés I, Oturan MA. Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry. *Chemical reviews*. 2009;109(12):6570–631.
 11. Meghlaoui FZ, Merouani S, Hamdaoui O, Bouhelassa M, Ashokkumar U. Rapid catalytic degradation of refractory textile dyes in Fe(II)/chlorine system at near neutral pH: Radical mechanisms, chlorine dioxide radical anion ($\text{Cl}_2^{\bullet-}$)-mediated transformation pathways and impact of environment matrices. *Separation and Purification Technology*. 2019;227:115685.
 12. Behin J, Akbari A, Mahmoudi M, Khajeh M. Sodium hypochlorite as an alternative to hydrogen peroxide in Fenton process for industrial scale. *Water Research*. 2017;121:120–128.
 13. Kałuzna-Czaplińska J, Gutowska A, Józwiak WK. The chemical degradation of C.I. Acid Brown 349 in aqueous solution using hydrogen peroxide and sodium hypochlorite and its implications for biodegradation. *Dyes and Pigments*. 2010;87(1):62–68.

14. Candeias LP, Stratford MRL, Wardman P. Formation of hydroxyl radicals on reaction of hypochlorous acid with ferrocyanide, a model IRON(II) complex. *Free Radical Research*. 1994;20(4):241–249.
15. Folkes LK, Candeias LP, Wardman P. Kinetics and mechanisms of hypochlorous acid reactions. *Archives of Biochemistry and Biophysics*. 1995;323(1):120–126.
16. Tarr MA. *Chemical degradation methods for wastes and pollutants*. (Tarr MA, ed.). New York, USA: Marcel Dekker, Inc.; 2003.
17. Remucal CK, Manley D. Emerging investigators series: The efficacy of chlorine photolysis as an advanced oxidation process for drinking water treatment. *Environmental Science: Water Research and Technology*. 2016;2(4):565–579.
18. Laat J DE, Stefan M. UV/chlorine process. In: Stefan MI, ed. *Advanced oxidation processes for water treatment*. London, UK: IWA Publishing; 2017:383–428.
19. Xue W, Lin Z, Chen H, Lu C, Lin JM. Enhancement of ultraweak chemiluminescence from reaction of hydrogen peroxide and bisulfite by water-soluble carbon nanodots. *Journal of Physical Chemistry C*. 2011;115(44):21707–21714.
20. Chen H, Lin L, Lin Z, Guo G, Lin JM. Chemiluminescence Arising from the decomposition of peroxymonocarbonate and enhanced by CdTe quantum dots. *Journal of Physical Chemistry A*. 2010;114(37):10049–10058.
21. Prutz WA. Hypochlorous Acid Interactions with Thiols , Nucleotides , DNA , and Other Biological Substrates. *Archives of Biochemistry and Biophysics*. 1996;332(1):110–120.
22. Wu Z, Guo K, Fang J, Yang XX, Xiao H, Hou S, Kong X, Shang C, Yang XX, Meng

- F, Chen L. Factors affecting the roles of reactive species in the degradation of micropollutants by the UV/chlorine process. *Water Research*. 2017;126:351–360.
23. Neta P, Huie RE, Ross AB. Rate constants for reactions of inorganic radicals in aqueous solution. *J. Phys. Chem. Ref. Data*. 1988;17(3):1027–1284.
24. Kong X, Li X, Wu Z, Ren Z, Guo K, Fang J, Hua Z, Hou S, Hua Z, Li X, Fang J, Wu Z, Ren Z, Guo K, Fang J, et al. Degradation of lipid regulators by the UV/chlorine process: Radical mechanisms, chlorine oxide radical (ClO•)-mediated transformation pathways and toxicity changes. *Water Research*. 2018;137:242–250.
25. Fang J, Fu Y, Shang C. The roles of reactive species in micropollutant degradation in the UV/free chlorine system. *Environmental Science and Technology*. 2014;48(3):1859–1868.
26. Qin L, Lin YL, Xu B, Hu CY, Tian FX, Zhang TY, Zhu WQ, Huang H, Gao NY. Kinetic models and pathways of ronidazole degradation by chlorination, UV irradiation and UV/chlorine processes. *Water Research*. 2014;65:271–281.
27. Deborde M, Gunten U Von. Reactions of chlorine with inorganic and organic compounds during water treatment — Kinetics and mechanisms : A critical review. *Water Research*. 2008;42:13–51.
28. Sanz J, Lombraña JI, De Luis AM, Ortueta M, Varona F. Microwave and Fenton's reagent oxidation of wastewater. *Environmental Chemistry Letters*. 2003;1(1):45–50.
29. Bendjama H, Merouani S, Hamdaoui O, Bouhelassa M. Efficient degradation method of emerging organic pollutants in marine environment using UV/periodate process: Case of chlorazol black. *Marine Pollution Bulletin*. 2018;126(September):557–564.

30. Alfassi ZB, Huie RE, Mosseri S, Neta P. Kinetics of one-electron oxidation by the ClO radical. *International Journal of Radiation Applications and Instrumentation. Part.* 1988;32(1):85–88.
31. Buxton G V., Bydder M, Salmon GA, Williams JE. The reactivity of chlorine atoms in aqueous solution. Part III. The reactions of Cl• with solutes. *Physical Chemistry Chemical Physics.* 2000;2(2):237–245.
32. Buxton G V., Bydder M, Arthur Salmon G. Reactivity of chlorine atoms in aqueous solution Part 1 The equilibrium $\text{Cl} + \text{Cl}_2 \rightleftharpoons \text{Cl}_2^-$. *Journal of the Chemical Society, Faraday Transactions.* 1998;94(5):653–657.
33. Buxton G V., Greenstock CL, Helman WP, Ross AB. Critical review of rate constants for reactions of hydrated Electrons, hydrogen atoms and hydroxyl radicals ($\bullet\text{OH}/\text{O}^-$) in aqueous solution. *Journal of Physical and Chemical Reference Data.* 1988;17(2):515–886.

Table 1. Reaction mechanism for Fe(III)/chlorine system (Ref. 11, except reaction 1 and 2).

n°	Reaction	Rate constants ($M^{-1}s^{-1}$)
1	$Fe(III) + HClO \rightarrow Fe(II) + ClO^{\bullet} + H^+$	-
2	$Fe(II) + HClO \rightarrow Fe(III) + ^{\bullet}OH + Cl^{-}$	$\sim 10^4$
3	$Fe(II) + HClO \rightarrow Fe(III) + Cl^{\bullet} + OH^{-}$	$\sim 10^4$
4	$^{\bullet}OH + HClO \rightarrow ClO^{\bullet} + H_2O$	2×10^9
5	$Cl^{\bullet} + HClO \rightarrow ClO^{\bullet} + H^+ + Cl^{-}$	3×10^9
6	$Cl^{\bullet} + Cl^{-} \rightleftharpoons Cl_2^{\bullet-}$	$k_7 = (0.65-2.1) \times 10^{10} M^{-1}s^{-1}$, $k_{-7} = 6 \times 10^4 M^{-1}s^{-1}$
7	$Cl^{\bullet} + H_2O \rightarrow HClO^{\bullet-} + H^+$	2.5×10^5
8	$HClO^{\bullet-} \rightleftharpoons ^{\bullet}OH + Cl^{-}$	$k_8 = 6.1 \times 10^9 M^{-1}s^{-1}$, $k_{-8} = 4.3 \times 10^9 M^{-1}s^{-1}$
9	$HClO^{\bullet-} + H^+ \rightarrow Cl^{\bullet} + H_2O$	2.1×10^{10}
10	$HClO^{\bullet-} + Cl^{-} \rightarrow Cl_2^{\bullet-} + OH^{-}$	1×10^5
11	$Cl_2^{\bullet-} + H_2O \rightarrow Cl^{-} + HClO^{\bullet-} + H^+$	1×10^5
12	$Cl_2^{\bullet-} + ^-OH \rightarrow Cl^{-} + HClO^{\bullet-}$	1×10^5
13	$Fe^{2+} + ^{\bullet}OH \rightarrow Fe^{3+} + OH^{-}$	3.2×10^8
14	$Fe^{2+} + Cl_2^{\bullet-} \rightarrow Cl^{-} + FeCl^{2+}$	1.4×10^7
15	$Cl_2^{\bullet-} + Cl_2^{\bullet-} \rightarrow Cl_2 + 2 Cl^{-}$	6.3×10^8
16	$^{\bullet}OH + ^{\bullet}OH \rightarrow H_2O_2$	5.5×10^9
17	$Cl_2^{\bullet-} + ^{\bullet}OH \rightarrow HClO + Cl^{-}$	1×10^9
18	$Cl_2^{\bullet-} + Cl^{\bullet} \rightarrow Cl_2 + Cl^{-}$	2.1×10^9
29	$Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$	8.8×10^7
20	$ClO^{\bullet} + ClO^{\bullet} \rightarrow Cl_2O_2$	7.5×10^9
21	$ClO^{\bullet} + Cl^{\bullet} \rightarrow HCl + HClO_3$	-

Table 2. Reactivity between scavengers and radicals in the Fe(II)/chlorine system.

Scavenger	Rate constants k ($\text{M}^{-1} \text{s}^{-1}$)			
	$\bullet\text{OH}$	$\text{Cl}\bullet$	$\text{Cl}_2\bullet^-$	$\text{ClO}\bullet$
Nitrobenzene (NB)	3.9×10^9 ^a	<i>neg.</i> ^a	<i>neg.</i> ^a	<i>neg.</i> ^b
Benzoic acid (BA)	1.8×10^9 ^a	1.8×10^{10} ^a	$(0.2-1.8) \times 10^6$ ^{a,b}	$< 3 \times 10^6$ ^c
Azide ions (N_3^-)	1.4×10^{10} ^d	5.2×10^9 ^e	$(0.5-1.2) \times 10^9$ ^{d,f}	2.5×10^8 ^c
t-butanol	6×10^8 ^d	3×10^8 ^d	0-700 ^g	1.3×10^7 ^d
Phenol	6×10^8 ^h	$(0.8-2.5) \times 10^9$	$(2.5-5) \times 10^{8b}$	NA*

a) Ref. ¹⁷, b) Ref. ¹⁸, c) Ref. ³⁰, d) Ref. ²², e) Ref. ³¹, f) Ref. ²³, g) Ref. ³², Ref. ³³

* Not available, but phenol mostly reacts with all radicals with high rate constant ²³

Fig. 1. Effect of initial Fe(III) concentration on the removal kinetics of RG12 with Fe(III)/chlorine system (conditions: $V = 200$ mL, $C_0 = 30$ mg/L ($16.32 \mu M$), $[chlorine]_0 = 250 \mu M$, $[Fe(III)]_0 = 0-100 \mu M$, pH 4, temperature = 20 ± 2 °C). The insert represents the removed amount (in mg/L) after 30 s upon chlorine and Fe(III)/chlorine treatments as well as the enhancement index vs. initial Fe(III) dosage.

Fig. 2. Removal efficiency at 30 s for several dyes under chlorine alone and Fe(III)/chlorine process (conditions: $C_0 = 16.32 \mu\text{M}$, $[\text{Fe(III)}]_0 = 50 \mu\text{M}$, $[\text{chlorine}]_0 = 250 \mu\text{M}$, pH 4, temperature: $20 \pm 2 \text{ }^\circ\text{C}$).

Fig. 3. Comparison of the effect of Fe(III)/chlorine and Fe(II)/chlorine treatments on the removal kinetics of RG12 (conditions: $V = 200$ mL, $C_0 = 30$ mg/L ($16.32 \mu\text{M}$), $[\text{Fe(III)}]_0 = [\text{Fe(II)}]_0 = 50 \mu\text{M}$, $[\text{chlorine}]_0 = 250$ mM, pH 4, temperature: 20 ± 1 °C).

Fig. 4. Influence of specific radical scavengers on the degradation kinetics of RG12 by Fe(III)/HClO process (conditions: $V = 200$ mL, $C_0 = 30$ mg/L ($16.32 \mu\text{M}$), $[\text{chlorine}]_0 = 250 \mu\text{M}$, $[\text{Fe(III)}]_0 = 50 \mu\text{M}$, pH 4, temperature = 20 ± 2 °C).

Fig. 5. Effect of initial chlorine concentration on the removal kinetics of TB upon Fe(III)/chlorine system (conditions: $V = 200$ mL, $C_0 = 30$ mg/L ($16.32 \mu\text{M}$), $[\text{chlorine}]_0 = 25$ - $1000 \mu\text{M}$, $[\text{Fe(III)}]_0 = 50 \mu\text{M}$, pH 4, temperature = 20 ± 2 °C). The insert (Fig. 5b) represents the removed amount (in mg/L) after 30 s upon chlorine and Fe(III)/chlorine treatments as well as the enhancement index vs. initial chlorine dosage.

Fig. 6. Effect of initial solution pH on the removal kinetics of RG12 upon Fe(III)/chlorine system (conditions: $V = 200$ mL, $C_0 = 30$ mg/L ($16.32 \mu\text{M}$), $[\text{Fe}^{2+}]_0 = 50 \mu\text{M}$, $[\text{chlorine}]_0 = 250 \mu\text{M}$, pH 3–7, temperature: 20 ± 1 °C). The insert (Fig. b) represents the removed amount (in mg/L) after 30 s upon chlorine and Fe^{2+} /chlorine treatments as well as the enhancement index vs. initial solution pH.

Fig. 7. Effect of liquid temperature on the removal kinetics of RG12 upon Fe(III)/chlorine system (conditions: $V = 200$ mL, $C_0 = 30$ mg/L ($16.32 \mu\text{M}$), $[\text{chlorine}]_0 = 250 \mu\text{M}$, $[\text{Fe(III)}]_0 = 50 \mu\text{M}$, pH 4, temperature = 10-50 °C). The insert represents the removed amount (in mg/L) after 30 s upon chlorine and Fe^{2+} /chlorine treatments as well as the enhancement index vs. liquid temperature.

Fig. 8. Effect of initial RG12 concentration on the removal kinetics upon Fe(III)/chlorine system (conditions: $V = 200$ mL, $C_0 = 30$ mg/L ($16.32 \mu\text{M}$), $[\text{chlorine}]_0 = 250 \mu\text{L}$, $[\text{Fe(III)}]_0 = 50 \mu\text{M}$, pH 4, temperature = 20 ± 1 °C). The insert represents the removed amount (in mg/L) after 30 s upon chlorine and Fe(III)/chlorine treatments as well as the enhancement index vs. initial RG12 concentration.

Fig. 9. Salts effect on RG12 removal after 30 s of treatment with Fe(III)/chlorine (conditions: $C_0 = 30 \text{ mg/L}$ ($16.32 \mu\text{M}$), $[\text{HClO}]_0 = 250 \mu\text{L}$, $[\text{Fe}^{2+}]_0 = 50 \mu\text{M}$, $[\text{salts}]_0 = 0\text{-}50 \text{ mM}$, pH 4 except for NaHCO_3 (pH 8.5) , temperature = $20 \pm 2 \text{ }^\circ\text{C}$).

Fig. 10. Impact of humic acid and surfactants on RG12 removal after 30 s of treatment with Fe(III)/chlorine (conditions: $C_0 = 30$ mg/L ($16.32 \mu\text{M}$), $[\text{HClO}]_0 = 250 \mu\text{L}$, $[\text{Fe}^{2+}]_0 = 50 \mu\text{M}$, $[\text{surf}]_0 = 1\text{-}100 \mu\text{M}$, $[\text{HA}]_0 = 5\text{-}20$ mg/L, pH 4 except for NaHCO_3 (pH 8.5), temperature = 20 ± 2 °C).

Minerva Access is the Institutional Repository of The University of Melbourne

Author/s:

Meghlaoui, FZ;Merouani, S;Hamdaoui, O;Alghyamah, A;Bouhelassa, M;Ashokkumar, M

Title:

Fe(III)-catalyzed degradation of persistent textile dyes by chlorine at slightly acidic conditions: the crucial role of Cl(2)(BLACK CIRCLE-)radical in the degradation process and impacts of mineral and organic competitors

Date:

2020-08-02

Citation:

Meghlaoui, F. Z., Merouani, S., Hamdaoui, O., Alghyamah, A., Bouhelassa, M. & Ashokkumar, M. (2020). Fe(III)-catalyzed degradation of persistent textile dyes by chlorine at slightly acidic conditions: the crucial role of Cl(2)(BLACK CIRCLE-)radical in the degradation process and impacts of mineral and organic competitors. ASIA-PACIFIC JOURNAL OF CHEMICAL ENGINEERING, 16 (1), <https://doi.org/10.1002/apj.2553>.

Persistent Link:

<http://hdl.handle.net/11343/276098>