Efficient decolorization of Malachite Green in the Fenton reaction catalyzed by [Fe(III)-salen]Cl complex

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HIGHLIGHTS

► Fe(III)-salenCl complex was successfully used in the treatment of Malachite Green.
► 3.5 folds reaction speed and a little higher decolorization rate were obtained.
► Main active oxidation specie was confirmed and the reaction mechanism was deduced.
► The decolorization of Malachite Green obeyed the pseudo-first order kinetics.
► The pseudo-activated energy was calculated and compared.

ABSTRACT

The catalysis effect of [Fe(III)-salen]Cl complex on the decolorization and degradation of Malachite Green in the Fenton system was investigated in this study. A significant decolorization enhancement was observed in the presence of only trace amount of the complex without additional equipment or external energy. The effects of reaction parameters were studied and the results showed that the increase of [Fe(III)-salen]Cl complex, molar ratio of salen ligand to Fe(III) and initial concentration of H2O2 favor the increase of decolorization rate. The increase of initial concentration of the dye leads to the decrease of decolorization rate and the optimum pH was the original pH of Malachite Green solution. Under the optimal condition, the decolorization and TOC removal rates after 24 min treatment were 97.94% and 54.35% respectively. Hydroxyl radical was identified as the main active oxidant species in the [Fe(III)-salen]Cl complex catalyzed Fenton system. The degradation intermediates of Malachite Green were analyzed and a possible reaction mechanism was proposed. The decolorization of Malachite Green obeyed the pseudo-first order equation and the activation energy was calculated by the related kinetic constants, which was only 49.13% of Fe(III) Fenton system.

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1. Introduction

Synthetic dyes are consumed widely in textile industry and it is estimated that more than 700,000 t dye wastewater is discharged annually [1]. Most dyes are difficult to be degraded due to their complex and stable aryl structures and the environmental contamination of dye pollutants is becoming an overwhelming problem all over the world [2]. In the past years, conventional chemical and physical methods have been the main techniques to remove the dye pollutants from wastewater, such as adsorption using activated carbon, coagulation by chemical agents, reverse osmosis, ozone oxidation and hypochlorite oxidation [3–7]. However, these methods are usually non-destructive, inefficient, costly and resulted in the production of secondary pollution [8]. It is necessary to develop novel and cost-effective technologies to treat the dye wastewater.

Advanced oxidation technologies have been accepted as efficient ways for the degradation of toxic and refractory organics [9–11]. Especially, Fenton processes have been proved as one of the best methods for the control of organic pollution, in which cheap and environmentally friendly reagents are employed [12]. The generation of hydroxyl radical in Fenton process are described in the following equations [13].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad k_1 = 58 \text{ mol}^{-1} \text{ dm}^3 \text{s}^{-1}$$

(1)
Fenton reactions. An effective ligand is still the bottle-neck of complex catalyzed reaction on the Fenton reaction, such as EDTA[10], 5-sulfosalicylic acid[13] and citrate[16]. But the research is still limited and the selection of ligands was also reported with little improving effect and the oxidative degradation of organics.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}_2^- + \text{H}^+ \quad (3)
\]

According to Eqs. (1)–(3), Fe\(^{2+}\) is oxidized to Fe\(^{3+}\) and then regenerated by the reaction with H\(_2\)O\(_2\). Unluckily, the reaction rate of Eq. (3) is much slower than that of Eq. (1). The Fe\(^{2+}\) ions are quickly consumed but slowly regenerated and the resulting low concentration of Fe\(^{3+}\) makes the Fenton reaction slow down[14]. So enhancing the regenerated rate of Fe\(^{2+}\) ion is the key problem in the traditional Fenton reaction. Recently Gupta et al. have reported the tetraamidomacroyclic chelating agent as an effective catalyst to transform Fe(III) into Fe(II) for Fenton reactions[15]. Some other ligands were also reported with little improving effect on the Fenton reaction, such as EDTA[10], 5-sulfosalicylic acid[13] and citrate[16]. But the research is still limited and the selection of an effective ligand is still the bottle-neck of complex catalyzed Fenton reactions.

Salen is one of the good ligands for many metals, such as Fe\(^{3+}\), Fe\(^{2+}\), Co\(^{3+}\) and Cu\(^{2+}\). The complex of salen ligand and Fe(III) has been known as an effect catalyst for the C–C cross coupling reaction[17] and many other catalytic processes, such as the oxidation of organic sulfides[18] and the aerobic epoxidation of styrene catalyzed by [Fe(III)-salen]Cl complex (Fig. 1) [19]. Therefore, the [Fe(III)-salen]Cl complex would possibly be a potent catalyst for the oxidative degradation of organics.

Malachite Green is an important dye and is widely used in textile industry. If discharged directly into streams, it will affect the aquatic lives and cause detrimental effects on the liver, gill, kidney, intestine, gonads and pituitary gonadotrophic cell of casualty[20]. Therefore, its removal from wastewater is of significance. The purpose of this study is to investigate the trace Fe(III)-salen]Cl complex Fenton system for decolorization and degradation of Malachite Green aqueous solution. The effect of each reagent was discussed and reaction parameters in [Fe(III)-salen]Cl complex Fenton system were evaluated, such as initial concentration of dye, hydrogen peroxide and [Fe(III)-salen]Cl complex, and the molar ratio of salen ligand to total iron. A comparison between the [Fe(III)-salen]Cl complex Fenton system and older Fe(III) Fenton system had been discussed to find the advantage of new system on reaction effect, reaction time and mineralization degree. In order to evaluate the practical applicability of the new system, a possible reaction mechanism and the degradation route of Malachite Green was proposed, reaction activation energy was confirmed and the reaction kinetics was investigated.

2. Materials and methods

2.1. Materials

All chemicals used were analytical grade and without further purification. Malachite Green was supplied by Shanghai Chemical reagent Ltd. Co (Shanghai, China), \(\text{H}_2\text{O}_2\) (30 wts%), \(\text{FeC}_3\text{H}_7\text{O}_4\), ethylenediamine, salicylaldehyde, t-butanol and ethanol were supplied by Sinopharm Chemical reagent Ltd. Co (Shanghai, China). Distilled water was used throughout.

2.2. Experimental methods

2.2.1. Synthesis of salen ligand

Ethanol (150 mL), ethylenediamine (3 g, 50 mmol) and salicylaldehyde (12.2 g, 100 mmol) were added into a 250 mL flask one by one and the resulting mixture was refluxed for another 4 h. The reaction mixture was then cooled to r.t. (25 °C), the resulting suspension was filtered and the yellow solid was washed with 50 mL of ethanol. After drying in vacuo, the target product salen ligand was obtained (12.3 g, Yield = 92%, \(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\), FW: 268.31).

2.2.2. Preparation of [Fe(III)-salen]Cl complex aqueous solution

The salen ligand was added to FeCl\(_3\) aqueous solution (0.5 mol/L) with varied mole ratio and the mixture was stirred by magnetic stirrer for 6 h to keep the ligand chelate with Fe\(^{3+}\) completely. The complex could also be obtained by placing the mixture of two materials overnight. The resulting solution was stored in a sealed bottle and ready for use in the degradation reaction.

2.2.3. Decolorization reaction of malachite green

The experiments were carried out in a conical flask (250 mL) with magnetic stirring. 100 mL of Malachite Green solution in certain concentration, certain amount of [Fe(III)-salen]Cl complex aqueous solution and \(\text{H}_2\text{O}_2\) were added into the conical flask. For the optimization experiment of pH situation, the addition step for the pH adjustment with HCl/\(\text{H}_2\text{O}\) (0.1 M) or NaOH (0.1 M) was needed. The conical flask was then sealed with parafilm and the mixture was stirred on the magnetic stirrer. At given time intervals, reaction mixture samples (1 mL) were taken with a disposable syringe, quenched with t-butanol and filtered with a 0.45 μm PES filtering film. The filtrate was then analyzed using a UV–VIS spectrophotometer immediately and the mixture should be diluted with distilled water when the absorbance exceeded the range of calibration curve.

2.3. Sample analysis

The pH value of the solutions was measured by a digital pH meter (Sartorius, Germany). The UV–VIS absorption spectra of Malachite Green were recorded from 220 to 800 nm using a Cary 50 UV–VIS spectrophotometer (Varian, USA) with a spectrometric quartz cell (1 cm path length), and the maximum absorption wavelength (\(\lambda_{\text{max}}\)) of Malachite Green was determined as 618 nm. Therefore, the concentration of Malachite Green in the reaction mixture at different reaction time was measured by the absorption intensity at \(\lambda_{\text{max}} = 618\) nm. A calibration curve was obtained by measuring the absorption spectra of standard Malachite Green aqueous solution with known concentrations and the reaction mixture samples should be diluted with distilled water when the absorbance exceeded the range of calibration curve. Total organic carbon was determined using liquid TOC II (Elementar, Germany) to evaluate the degree of mineralization of Malachite Green dye. For the determination of total organic carbon, the reaction mixture samples were analyzed directly by TOC analysis instrument, without the addition of t-butanol to avoid the interference. The intermediates of degradation of Malachite Green were detected by GC–MS. Electron impact mass spectra were obtained with an Agilent Trace GC 5975C system coupled to a quadrupole detector. The GC was equipped with an ion source at temperature of 220 °C and with El ionization at 70 eV. The weight percent of iron element in the complex molecule was determined using Atomic Absorption Spectrophotometer (AAS) model AA6650 (Shimadzu, Japan). The \(^{1}H\) NMR and \(^{13}C\) NMR spectrum were recorded at 295 °K on a Bruker AVIII 600 MHz nuclear magnetic resonance (Bruker, Bremen, Germany) in DMSO-d6 and was calibrated with tetramethylsilane (TMS) as the internal reference.
3. Results and discussion

3.1. Complex characterization

To confirm the complex molecule structure, the structure of ligand and the weight percent of iron element were confirmed by NMR and AAS (atomic absorption spectrometry), and the structure of complex was shown in Fig. 1. The \(^1\)H NMR and \(^{13}\)C NMR of ligand was analyzed as below. \(^1\)H NMR: 13.38 (s, 2H, –OH), 8.58 (s, 2H, –C=N), 7.42(d, 2H, –CH), 7.33–7.30 (m, 2H, –CH), 6.89–6.85 (m, 4H, –CH), 3.92 (s, 4H, –CH₂). \(^{13}\)C NMR: 167.41 (C–OH), 161.05 (–CH=N), 132.84(–CH=), 132.14(–CH=), 119.07(–C=), 119.04(–CH=), 116.95(–CH=), 59.25 (–CH₂–N). The weight percent of iron element was 15.62% (AAS) and the theoretical percent was also 15.62%.

3.2. Decolorization effects of Malachite Green in different processes

In order to demonstrate the effect of [Fe(III)-salen]Cl complex in the decolorization of Malachite Green, comparative experiments were carried out in single H₂O₂ system, single [Fe(III)-salen]Cl complex system, FeCl₃/H₂O₂ system and [Fe(III)-salen]Cl complex/H₂O₂ Fenton reaction system, respectively. All experiments were conducted in the same reactor and under the same operating conditions. As shown in Fig. 2, only slight decolorization of Malachite Green was observed after 90 min with the hydrogen peroxide alone (7.84%) or [Fe(III)-salen]Cl complex alone (3.16%). This phenomenon can be explained by the fact that hydrogen peroxide or [Fe(III)-salen]Cl complex itself cannot produce the hydroxyl radical which is a stronger oxidant and can oxidize most organic compounds. Compared with the single reaction of H₂O₂ and [Fe(III)-salen]Cl complex, after 24 min, decolorization rate of Malachite Green was a little higher in the FeCl₃/H₂O₂ reaction system and attained 14.78%. After 80 min, the decolorization rate could reach to a satisfactory amount, 93.56%, which was the max decolorization rate (97.94%) of FeCl₃/H₂O₂ system. This indicated the great catalytic ability of the complex, formed from FeCl₃ and salen ligand, to the hydrogen peroxide activation.

3.3. Active oxidant species

It was reported that there were two possible active oxidant species in the presence of ligand [10,18], the Fe (IV) species and hydroxyl radical, and the latter could be easily quenched by the radical inhibitor. The t-butanol is well known as free radical inhibitor and was wildly used to quench the hydroxyl radical reactions [21,22]. To evaluate the active oxidant species in [Fe(III)-salen]Cl complex Fenton system, t-butanol (0.05 mol/L) was applied and the removal rate of Malachite Green decreased from 97.94% to 11.21%, indicating that the hydroxyl radical was the main active oxidant species in the reaction. Larger amount of t-butanol (0.1 mol/L) was then applied to confirm that the amount of t-butanol was enough for the quenching of all hydroxyl radical and the same decolorization rate was obtained (Fig. 3). On the other side, Fe(IV) species have been reported as the active oxidant species in the oxidation reaction of sulfides catalyzed by Fe(III)-salen complex and the absorbance within the range of 550–750 nm on UV–VIS spectrum was used to analyzed the existence of Fe(IV) species [18]. In our experiment, a little absorbance increase could also be found within the range of 550–750 nm, by mixing the complex with H₂O₂ aqueous solution, which could be due to the formation of Fe(IV) species. So, it could be confirmed that small amount of Fe (IV) species may have little contribution to the decolorization of Malachite Green (11.21%).

3.4. Effect of reaction parameters on the decolorization of Malachite Green in the [Fe(III)-salen]Cl complex/hydrogen peroxide reaction system

3.4.1. Effect of the initial concentration of Malachite Green

To investigate the effect of the initial concentration of Malachite Green on the dye decolorization in the [Fe(III)-salen]Cl complex system.
complex/hydrogen peroxide reaction system, the initial concentration ranged from 50 mg/L to 200 mg/L was examined and the results are shown in Fig. 4. Among four initial Malachite Green concentrations, the decolorization of Malachite Green decreased with the increase of initial concentration of dye, keeping other reaction conditions constant. After a treatment for 24 min, the decolorization rate ranged from 98.82% to 15.13% when the initial concentration of Malachite Green varied from 50 mg/L to 200 mg/L. When the initial concentration of Malachite Green was changed from 50 mg/L to 100 mg/L, the decolorization rate is similar and only a decrease of 0.58% was found. But a notable decrease (98.82–40.90%) could be found when the initial concentration was increased from 100 mg/L to 150 mg/L. So the concentration of 100 mg/L was used as the optimum initial concentration. Under the catalysis of \([\text{Fe(III)}\text{-salen}]\text{Cl} \) complex, the hydrogen peroxide was mainly degraded to hydroxyl radical, which degrade the Malachite Green and the intermediates of reaction in the next step. Since the concentration of catalyst and oxidant were constant, we deduced that the total amount of active oxidant species would happen, except for the sufficient decolorization of Malachite Green [23–25].

3.4.2. Effect of the initial concentration of hydrogen peroxide

Hydrogen peroxide was the precursor of the active oxidant species, which degrade the reaction substrate directly. The amount of hydrogen peroxide would influence the concentration of active oxidant species and was an important parameter in the Fenton reaction process [26]. To determine the influence of the initial hydrogen peroxide concentration on the decolorization of Malachite Green, the initial hydrogen peroxide concentration was varied from 1 mmol/L to 15 mmol/L and the results were shown in Fig. 5. With the increase of hydrogen peroxide concentration from 1 mmol/L to 10 mmol/L, the decolorization rate increased from 35.28% to 97.94% after 24 min. This is due to that more active oxidant species would form in the presence of high concentration of hydrogen peroxide. However, when hydrogen peroxide concentration varied from 10 mmol/L to 15 mmol/L, there was no significant variation in the color removal and the decolorization rate increased only from 97.94% to 98.04%. This means that the active oxidant species increased less, which was produced from hydrogen peroxide decomposition, when the oxidant exceeded the optimum dosage. This phenomenon can be explained by the reason that excessive hydrogen peroxide molecules could trap hydroxyl radical as shown in the following reactions [10]:

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{HO}_2 \\
\text{HO}_2 + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{O}_2
\end{align*}
\]

The oxidation potential of \(\text{HO}_2^-\) is much smaller than that of hydroxyl radical. So, it is important to control the initial concentration of hydrogen peroxide and to avoid the trapping action of excessive hydrogen peroxide.

3.4.3. Effect of the initial concentration of \([\text{Fe(III)}\text{-salen}]\text{Cl} \) complex

Iron ions was the initiator of traditional Fenton reaction, so the concentration of \([\text{Fe(III)}\text{-salen}]\text{Cl} \) complex would be important to this complex improved Fenton reaction. To evaluate the influence of \([\text{Fe(III)}\text{-salen}]\text{Cl} \) complex concentration on the decolorization of Malachite Green, a set of experiments were carried out by varying the concentration of \([\text{Fe(III)}\text{-salen}]\text{Cl} \) complex from 25 mmol/L to 40 mmol/L, with the ratio of salen ligand to total iron as 1:10. As shown in Fig. 6, the decolorization of Malachite Green increased from 35.79% to 97.94% with the increase of \([\text{Fe(III)}\text{-salen}]\text{Cl} \) complex concentration from 25 mmol/L to 35 mmol/L and the decolorization increased slightly when the \([\text{Fe(III)}\text{-salen}]\text{Cl} \) complex dosage increased from 35 mmol/L to 40 mmol/L after 24 min treatment. Based on the results, it could been confirmed that the optimum amount of \([\text{Fe(III)}\text{-salen}]\text{Cl} \) complex was 35 mmol/L, which is enough to catalyze the transformation of hydrogen peroxide to active oxidant species and keep a better decolorization effect. Since the amount of oxidant is constant, no more active species would been produced and no improvement on the decolorization could been found when the amount of \([\text{Fe(III)}\text{-salen}]\text{Cl} \) complex was over the 35 mmol/L. More complex will not improve the decolorization rate much more and is also less economic [27].

3.4.4. Effect of molar ratio of salen ligand to total iron

Salen ligand played an important role in the \([\text{Fe(III)}\text{-salen}]\text{Cl} \) complex Fenton reaction system and the addition of ligand could transform the free Fe(II) ion to \([\text{Fe(III)}\text{-salen}]\text{Cl} \) complex, which had better catalytical activity than free Fe(III) ion for the degradation
reaction. However, a great application of ligand in the industry was not feasible, since the synthesis process needed extra cost. In order to find the optimal usage amount of [Fe(III)-salen]Cl complex, experiments with different molar ratio of salan ligand to total iron were carried out and the results were shown in Fig. 7. When the molar ratio of salen ligand to total iron varied from 1:20 or 1:15 to 1:10, there was a middle increase from 76.87% or 85.53% to 97.94% on the decolorization of Malachite Green after 24 min, keeping the total iron concentration as 350 \( \text{mol/L} \). With the increase of salen ligand, the concentration of chelated [Fe(III)-salen]Cl complex would be higher, which would make the active oxidant species increase and also make the decolorization of dye increase. The decolorization was respectively 97.94% and 98.18% in the molar ratio of 1:10 and 1:5 after 24 min and more salen ligand could not notably increase the decolorization of Malachite Green. So, the optimal ratio of salen ligand to total iron for the new Fenton system was confirmed as 1:10.

3.4.5. Effect of initial pH

To investigate the influence of pH value on the decolorization of malachite green in [Fe(III)-salen]Cl complex Fenton reaction system, the pH of dye solution was adjusted from 3.97 (the original pH of the malachite green aqueous solution) to 3 or 5. Fig. 8 showed that the decolorization rates were similar at pH = 3 and 3.97 (99.67% and 99.51% respectively). However, the decolorization rate decreased rapidly to 75.78% at pH = 5. This was due to that the number of hydroxyl radicals available for decolorization of dye reduced when the pH value was greater than four, since the hydroxyl peroxide was unstable and partly decomposed to oxygen before the conversion to hydroxyl radicals, in this condition [1]. The best decolorization effect could be obtained at 3.97, so it is not necessary to adjust the pH with acid or base.

Based on the data in Section 3.4, the optimum condition of [Fe(III)-salen]Cl complex Fenton system for the degradation of 100 mg/L Malachite Green is confirmed as that [MG] = 100 mg/L, [Fe(III)-salen]Cl complex = 35 \( \text{mol/L} \), [H\(_2\)O\(_2\)] = 10 mmol/L, the molar ratio of salen ligand and Fe(III) = 1:10, pH = 3.97.

3.5. Mineralization and degradation products of Malachite Green

It is well known that decolorization of Malachite Green does not mean that it is completely mineralized. Parts of dye was probably only oxidized to the small molecular organic compounds. To investigate the degree of mineralization during the degradation of the Malachite Green in [Fe(III)-salen]Cl complex Fenton system, the value of TOC was determined and the TOC removal rate is calculated as below:

\[
\text{TOC removal (\%) = } \left( \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \right) \times 100
\]

As shown in Fig. 9, the TOC removal rate was lower than the corresponding decolorization rate. When the decolorization of dye was 97.94%, the TOC removal rate was only 54.35%. The chromophore of dye was destructed completely, but the organic pollutant was only partly oxidized to CO\(_2\) and H\(_2\)O and the intermediates of degradation contributed to the TOC value [23,28]. To determine the intermediate of Malachite Green in the [Fe(III)-salen]Cl complex Fenton reaction, degradation products were analyzed by GC–MS and the results were that the main intermediates were N,N-dimethylformamide, formic acid, dimethylamine and glutaraldehyde. Small amounts of 3-(hydroxymethyl)pentanedial, 3-(hydroxydiphenylmethyl)pentanedial, 3-(diphenylmethylen)pentanedial and 3-((4-(dimethylamino)phenyl)(phenyl)methylene)pentanedial were found in ppm lever. According to the main intermediates of Malachite Green analyzed by GC–MS, the possible degradation mechanism of Malachite Green was shown in Fig. 10.
First, the hydroxyl radical, converted from the hydrogen peroxide, attacked the C=N double bond to form the new C–O bond and unstable nitrogen radical. Under the attack of two other hydroxyl radicals, two C=C bonds were then broken down to form the intermediates (1 and 2). The aldehyde group in the intermediate (1) was then attacked by hydroxyl radical and the C=O double bond was opened to form the new C–O bond and unstable oxygen radical, which improved the C=N bond break to form the intermediates (3 and 4). On the other side, the intermediate (2) could also be degraded to intermediate (5) by the hydroxyl radical and the other product is the intermediate (6). Second, two C=C bonds in the structure of (6) were broken down by the hydroxyl radical to form the intermediate (7), which was converted to intermediate (8) under the attack of another hydroxyl radical. Finally, the intermediate (8) was degraded to CO₂ and H₂O, through a series of breaks on C=C bond.

3.6. UV–VIS absorption spectra analysis of malachite green in [Fe(III)-salen]Cl complex Fenton system

The UV–VIS absorption spectra of the dye solution in different reaction time were recorded to investigate the structural change of Malachite Green in [Fe(III)-salen]Cl complex Fenton system and the results are shown in Fig. 11. It is shown that the Malachite Green aqueous solution has three characteristic absorption bands. The maximum and the second absorption band is in the visible region, with the peak at 618 nm and 425 nm, which should be attributed to the extended chromophore, comprising all conjugated aromatic rings connected through the C=C, C=N double bond, and the third absorption band is at 315 nm in the ultraviolet region, which is due to the benzene ring structure of Malachite Green [29]. After initiation of the reaction, all the absorption peak became weaker along with the increase of reaction time and nearly disappeared after 24 min, which indicated that the chromophore, conjugated π system, was destroyed [30]. In order to clarify the possible interference effect of main intermediates, N,N-dimethylformamide, formic acid, dimethylamine and glutaraldehyde, the interaction experiments between intermediates and Malachite Green was studied. Each intermediate was mixed with Malachite Green one by one and the UV–VIS absorption spectra of the mixture were measured. The results are that the absorption peak of mixture is much similar with that of the pure Malachite Green solution, at the same mole concentration (see the details in supplementary material). No increase, decrease or wavelength shift of Malachite Green’s absorption could be found. So, the UV–VIS absorption spectra could be used to analyze the concentration of Malachite Green.

3.7. Proposed reaction mechanism

According to the results for the detection of active species, the degradation process of Malachite Green was mainly under the oxidation of hydroxyl radical. According to the literature, the addition of 5-sulfosalicylic acid or tetraamidomacrocyclic ligand could accelerate the transformation from Fe³⁺ to Fe²⁺ [13,15], improve the
transformation of hydrogen peroxide to hydroxyl radical and accelerate the Fenton reaction. So, we can deduce that the main reaction pathway was possibly as the following three steps. In the first step, Fe(III)-salen produced Fe2+ in the presence of H2O2. In the second step, Fe2+ reacted with H2O2 to produce Fe3+ and hydroxyl radical. Finally, the Malachite Green was oxidated to intermediates, CO2 and H2O, by hydroxyl radical. The addition of salen ligand improved the transformation from Fe3+ to Fe2+ and accelerated the degradation of Malachite Green at last. Besides, small parts of the [Fe(III)-salen]Cl complex was transferred to Fe(IV) species in the presence of hydrogen peroxide, which also had the ability to degrade Malachite Green. However, this reaction pathway had less contribution to the decolorization of Malachite green according to our experimental results.

3.8. Reaction kinetics and activation energy

The decolorization of Malachite Green at different temperatures obeyed the pseudo-first-order kinetic model and the results were show in Table 1. The temperature had positive effect on the decolorization of Malachite green in both Fe(III) Fenton and [Fe(III)-salen]Cl complex Fenton systems. The improvement of decolorization was observed with the increase of temperature from 20°C to 50°C, the corresponding increases of kobs from 0.00366 min⁻¹ to 0.02045 min⁻¹ in Fenton reaction and from 0.1763 min⁻¹ to 0.4151 min⁻¹ in [Fe(III)-salen]Cl complex Fenton system. In order to verify the catalysis of salen complex, the pseudo-activation energy (Ea) was calculated in both reaction and [Fe(III)-salen]Cl complex Fenton system. The Arrhenius equation was used to calculate Ea [31].

\[ k = A \times \exp(-\frac{E_a}{RT}) \]  

As shown in Fig. 12, two good linear correlation between ln(kobs) and 1/T were observed and the activation energy were calculated as 48.89 kJ/mol and 24.02 kJ/mol in Fenton reaction and [Fe(III)-salen]Cl complex Fenton system respectively. The compare of two activation energy showed that the addition of the salen ligand can reduce the activation energy (49.13% of Fe(III) Fenton system) and make the decolorization reaction more easy to be initiated.

4. Conclusions

In this study, [Fe(III)-salen]Cl complex Fenton system was established as an efficient process for decolorization of Malachite Green by enhancing the rate of Fe2+ regeneration. The intermediates were confirmed and a possible degradation mechanism of Malachite Green was proposed, which could be helpful for the tracking of degradation process. Compared to the older Fe(III) Fenton system, the [Fe(III)-salen]Cl complex Fenton system has several advantages, such as 6.6 times decolorization rate in 24 min, 3.5 folds reaction speed to reach the max decolorization and only 49% activation energy as that of Fe(III) Fenton system, which indicated the better catalytical effect of the complex and this efficient degradation reaction should be more significant and attractive for the removal of persistence organic contaminants. Through testing the processing parameters of the new system, it can be confirm that the decolorization was mainly affected by the amount of [Fe(III)-salen]Cl catalyst and H2O2 oxidant. The [Fe(III)-salen]Cl complex Fenton system was here newly developed and further studies need to be performed to make this method more useful, such as immobilization and recycling.

Acknowledgements

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Table 1

<table>
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<th>Reaction temperature (°C)</th>
<th>kobs (min⁻¹) in [Fe(III)-salen]Cl complex system</th>
<th>R²</th>
<th>kobs (min⁻¹) in FeCl3/H2O2 system</th>
<th>R²</th>
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Fig. 11. UV–VIS spectra absorption of Malachite Green during the reaction process.

Fig. 12. Arrhenius plot demonstrating temperature dependence of observed rate constant. [MG] = 100 mg/L, [Fe(III)-salen]Cl complex = 35 μmol/L, [H2O2] = 10 - 60 mmol/L, the molar ratio of salen ligand and Fe(III) = 1:10.
References


