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Degradation of organic pollutant in restaurant wastewater using the homogenous catalysis with Mn(II) and EDTA

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ABSTRACT

It can be seen that the objects of wastewater that need to be treated are quite diverse in types and complex in terms of reaction mechanisms. The methods mainly focus on the treatment of toxic organic compounds, especially phenols or plant protection agents in industrial wastewater, paper industry, food production, textile industry, printing industry... The activation of H_2O_2 and O_2 by complexes of transitional metal ions and suitable ligands creates oxidizing agents and ecologically healthy products. The intermediate substances arising in the activation process such as free radicals $OH^{\cdot}$, $O_2^{\cdot}$, $HO_2^{\cdot}$, ... can oxidize many compounds, especially the ability to attack the aroma of organic pollutants. In this paper, the results of research on treating organic pollution in restaurant wastewater with H_2O_2 are presented as a catalyst of complexes between Mn^{2+} ions and EDTA. The conditions including pH, EDTA/Mn^{2+}, the concentration of H_2O_2, Mn^{2+} were investigated to obtain the optimum conditions for improving COD treatment efficiency. This work proposes a method based on formation of the Mn(II)-EDTA complex, β=1; with the optimal conditions of other factors as following $[H_2O_2]_0$ = 0,75.10^{-3} mol/L; $[Mn(EDTA)]^{2}$- = 33,33 mol/L, pH=10.5; t = 15 minutes. The initial COD of 1025 mg/L decreased to 135 mg/L after the proposed procedure. The results provide solutions of homogeneous complex catalysts for domestic/restaurant and industrial wastewater treatment at room temperature and atmosphere.

Introduction

Restaurant wastewater is water that has been used for cleaning meats and vegetables, washing dishes, and cooking utensils, or cleaning the floor. The wastewater contains a high concentration of organic matters from the leftovers of food and soup which are made of oily flavorings such as soy sauce, seasoning, spice, etc. Nowadays, in Vietnam, many restaurants generate a large a mount of wastewaters daily, which consequently lead to various harmful impacts on the surrounding environment. In addition, the wastewater from restaurant and fast-food shops often has a high COD concentration and color [1]. It shows that the wastewater contains many organic substances which are difficult to biodegrade, causing pollution when discharged into nearby sources such as urban drainage systems, residential areas; rivers, streams, canals, ditches; lakes, ponds, lagoons ...they can affect groundwater, or drinking water through the

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percolation of contaminants in produced water into the water resources beneath the soil. Furthermore, the presence of oil and grease in the wastewater also tends to foul the storm drain and generates unpleasant odor. In recent years, besides methods such as adsorption, flocculation … the wastewater treatment method using homogeneous catalyst complex is known as an effective solution to treat toxic difficult-decomposing organic substances due to the process of creating a large amount of highly active intermediates, especially hydroxyl ($OH^{.}$) - capable of oxidizing most persistent organic compounds [2,3]. The conversion of transition metal ions such as Fe^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+} … into the homogeneous complexes formed from combining with a suitable ligand can expand the processing range at a wider pH range from the low pH level (3-4) to the high pH level and minimizes the amount of the used metal ions as well as H_2O_2 [2]. It is worthy to note that this is an improved method to expand the classic Fenton system in the environmental treatment processes [3].

For a long time, the removal efficiencies, and mechanisms for EDTA complexes has attracted a great attention. The molecule has two functional groups (–NH_2 and –COOH), they both show acidity and show basicity, and can form complexes with many transition metal ions. Some of the complexes are catalytic and have antibacterial and antifungal properties, thus, their complexes are widely used in many fields such as: microbiological analysis, medicine, agriculture, industry, especially in the field of industrial wastewater treatment. Complexation of EDTA with metal ions is determined by two functional groups –COOH and group –NH_2. The nitrogen atom in the –NH_2 group can give electrons to form a donor bond with metal ions. Meanwhile, H+ ions are also easily separated from the –COOH group to form –COO–, this group easily forms a covalent bond with metal ions through the oxygen atom. Therefore, EDTA can create ring complexes that are more stable with many metal ions [4].

This method involving Metal-EDTA complexes is highly recommended for a fast rate of pollutant removal, neat setup, straightforward operation, and low costs. Moreover, it is practically more effective in treating wastewaters containing small and light particles, which is usually observed in as oily restaurant wastewater. Hence, it is expected that the wastewater treatment method using homogeneous catalyst complex would be an ideal choice for treating restaurant wastewaters. The objective of the present study is to examine the feasibility of this method in treating restaurant wastewater and to determine the optimum operational conditions. In this paper, two research systems have been explored as follows:

Wastewater – Mn^{2+} - H_2O_2 (I)

Wastewater– EDTA- Mn^{2+} - H_2O_2 (II)

Experimental

The studied samples were collected according to TCVN 6663-1:2011 (ISO 5667-1:2006).

The wastewater sample's parameters which were determined both before and after the treatments include pH, COD according to TCVN 6491:1999 (ISO 6060:1989).

Chemicals

Manganese Sulfate Monohydrate ($MnSO_4.H_2O$): China
Ethylenediamine Tetraacetic Acid Disodium, EDTA $C_{10}H_{14}N_2O_8Na_2.H_2O$: GHTECH, China.
Hydrogen Peroxide , H_2O_2 30%: Xilong Scientific, China
HCl 10%, NaOH 10%, H_2SO_4 98%, Ag_2SO_4, $K_2Cr_2O_7$, $(NH4)_2Fe(SO4)_2.6H2O$, Feroin: Xilong Scientific, China.

Equipment for carrying experiments

COD Aqualytic AL125: AQUALYTIC, Germany.
pH meter: HACH-LANGE, Spain.
AREC.X Digital Hot Plate Stirrer: VELP, Italy

Results and discussion

The restaurant wastewater from a certain restaurant were collected after going through an extremely simple mechanical treatment system. For this type of wastewater, the initial COD value is usually very high (about 800-2000mg/l).

The high COD is mainly due to dissolved organic matters in the studied wastewater. Investigating the optimum conditions of the process by homogeneous complex method accompanying with the H_2O_2 decomposition to create OH• radicals [2,7] were focused on:

Investigate the effect of the ratio of β ([EDTA]/[Mn^{2+}]) on COD treatment efficiency in wastewater samples.

Investigate the effect of pH on COD treatment efficiency in wastewater samples.

Investigate the effect of complex concentration $[MnEDTA]^{2-}$ on COD treatment efficiency in wastewater samples.

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Investigate the effect of concentration $[H_2O_2]$ on COD treatment efficiency in wastewater samples.

Investigate the effect of reaction time on COD efficiency in wastewater samples.

It is clear that it is important to study the role of ion Mn^{2+} without/with the appropriate ligands in organic pollutant treatment by using H_2O_2 decomposition reaction. First, the system (I) was chosen to determine the efficiency of organic pollutants treatment without ligands.

Wastewater – Mn^{2+} - H_2O_2 (I)

The results of the studied system (I) showed that the treated wastewater has a change in COD_{out} value (1022 mg/L) is not significantly different from the original COD_{in} (1025 mg/L). In a relatively high pH environment, with large concentrations of $[Mn^{2+}]$, Mn^{2+} ions can be hydrolyzed to form hydroxides of different strengths, resulting in precipitation that causes the system to become cloudy and no longer homogeneous leading to terminate catalytic activities.

The effect of the ratio of [EDTA]/[Mn^{2+}] on COD treatment efficiency in wastewater samples

The experiment is conducted with the conditions: COD_{in}= 1025 mg/L, $[EDTA]_0$ = 16,67.10^{-5} mol/L; $[H_2O_2]_0$ = 1,5.10^{-3} mol/L; pH = 9,0; reaction time 10 minutes; the concentration $[Mn^{2+}]$ changes so that the ratio varied from 0,2.10^{-5} to 5,0.10^{-5} mol/L. The change of COD and treatment efficiency in wastewater samples according to the corresponding ratio of β is shown in Figure 1.

The obtained results in Figure 1 show that COD decreased gradually corresponding the increasing treatment efficiency when the ratio increases from 0,2 to 1,0 and reached the maximum at β = 1,0 with COD value equals 490 mg/l corresponds to a COD treatment efficiency of 52,2% (sample 10). As the concentration of $[Mn^{2+}]$ continued to decrease, the rate of β > 1 COD index in the samples increased gradually, the treatment efficiency decreased.

The above fluctuations can be explained as follows: When the rate increases, the ability to create complexes between Mn^{2+} and $[EDTA]^{4-}$ increases, leading to increased ability to form an active intermediate complex, pollutants are more oxidized.

Hence the COD of the samples decreases, the efficiency of the process increases. When β > 1, the process of complexing $[Mn(EDTA)]^{2-}$ is almost completely due to having passed the 1: 1 molar ratio on the other hand when β > 1, the residual $[EDTA]^{4-}$ becomes the agent increases the COD value, reduces the efficiency of the treatment process (compared to sample 10). Therefore, β = 1 was chosen as the optimal value and use to examine the next influencing factors.

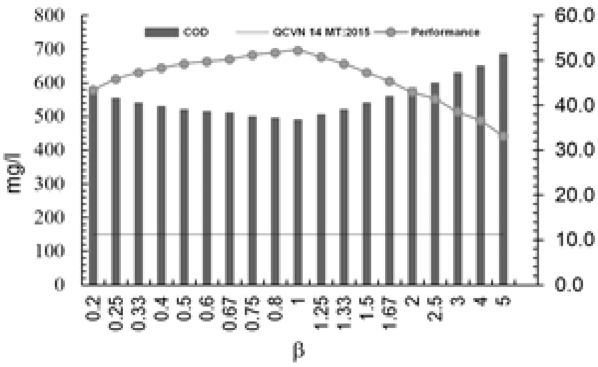

Figure 1: Effect of β on COD treatment performance of wastewater samples (QCVN 14-MT:2015: Vietnam National technical regulation on domestic wastewater)

Effect of pH on COD treatment efficiency in wastewater samples

The experiment was conducted under the following conditions: COD_{in}= 1025 mg/L, $[Mn^{2+}]_0$ = $[EDTA]_0$ = 16,67.10^{-5} mol/L; $[H_2O_2]_0$ = 1,5.10^{-3} mol/L, reaction time t = 10 minutes; the pH value changes from 7,5 to 12,5. The change of COD value and the efficiency of oxidation decomposition of organic matter with respect to the pH of the reaction medium are presented Figure 2.

Experimental results show that oxidation decomposition of organic compounds is greatly affected by pH. When pH increases, the decomposition efficiency of organic matter in wastewater increases and reaches the maximum value at pH = 10,5 with COD_{out} = 405 mg/l, the efficiency is 60,49%. As pH continuously increases, the efficiency of sample treatment decreases gradually.

The dependence of the oxidation of organic compounds on pH can be explained as follows: pH is one of the important factors in the complexing process, pH dictates the ability to create complexes and the constant of the tenacity of the complex. When pH <10,5, EDTA molecules containing functional groups $-NH_2$ easily accept proton H^+ to form $R-NH_3^+$, reducing the ability to create catalytic complexes with Mn^{2+}.

$$R - NH_2 + H^+ \rightleftharpoons R - NH_3^+$$

When the pH increases, the concentration of H^+

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decreases gradually, the above equilibrium will shift to the opposite direction creating favorable conditions for the formation of a catalytic complex $[MnEDTA]^{2-}$ and an increased active intermediate complex. As a result, the degradation efficiency of polluting organic matter increases and reaches a maximum at pH = 10,5. When pH>10,5, the concentration of OH^- in the solution increases, it favors conditions for the hydrolysis of Mn^{2+}, causing the complex to change gradually to the $Mn(OH)_2$ hydroxide form to precipitate, making the system lose its homogeneous and reduce catalytic activities of complexes, reducing oxidation capacity, thus reducing pollutant decomposition efficiency in wastewater.

Based on the experimental data in Figure 2, the optimal pH value of 10,5 was chosen to study other influencing factors on the next wastewater treatment process.

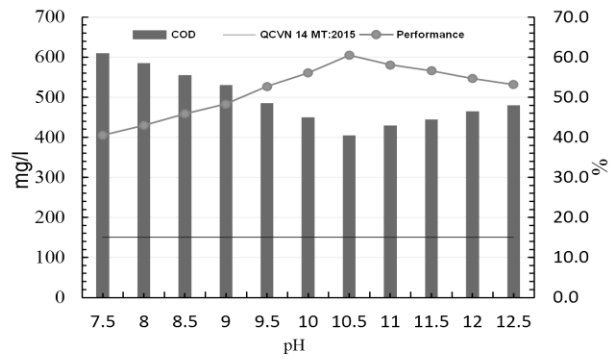

Figure 2: Effect of pH on COD treatment performance of wastewater samples (QCVN 14-MT:2015: Vietnam National technical regulation on domestic wastewater)

Effect of complex concentration $[Mn(EDTA)]^{2-}$ on process efficiency

The experiment was carried out in the following conditions: pH = 10,5; $[H_2O_2]_0$ = 1,5.10^{-3} mol/L; reaction time was t = 5 minutes; the complex concentration of $[Mn(EDTA)]^{2-}$ = 3,33.10^{-5} ÷ 333,33.10^{-5} mol/L, respectively. The results of the change and COD treatment efficiency were presented in Figure 3. As the concentration of complexes $[Mn(EDTA)]^{2-}$ increases from 3,33.10^{-5} to 33,3.10^{-5} mol/L, the amount of complexes present in the solution increases leading to the higher probability of collisions between ions to create more complexes and oxidation agents were also increased. The oxidation of organic compounds occurs more, the reaction speed is higher, thus, the treatment efficiency increases and later reaches a maximum with $[MnEDTA]^{2-}$ = 33,33.10^{-5} mol/L, COD_{out} value is 300 mg/L corresponding to an efficiency of 70,73%. After getting to the maximum, the concentration of complexes continues to increase, beside making complexes to catalyze the formation of $^{\cdot}OH$ radical, there is a remaining amount of complexes that affects the background solution as a results, the COD treatment efficiency decreased. Therefore, $[Mn(EDTA)]^{2-}$ = 33,33.10^{-5} mol/L is the optimal concentration used for next experiments.

Effect of concentration $[H_2O_2]_0$ on treatment efficiency

The experiment is conducted in the following conditions: pH = 10,5; $[Mn(EDTA)]^{2-}$ = 33,33.10^{-5} mol/L; the reaction time t = 5 minutes; H_2O_2 concentration changes from 0,15.10^{-3} ÷ 30,10^{-3} mol/L. The change of COD value and the efficiency of the oxidation decomposition of organic pollutants according to the concentration $[H_2O_2]_0$ is shown in Figure 3.

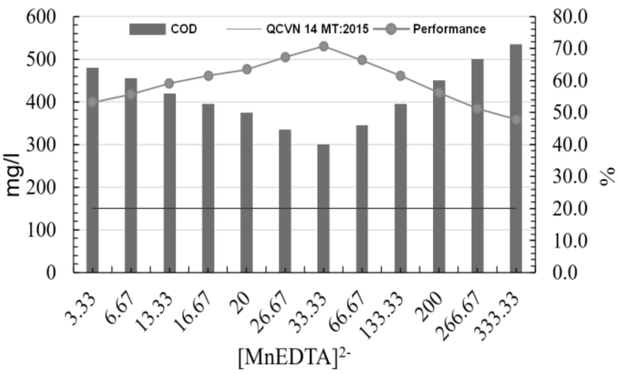

Figure 3: Effect of catalytic complex on COD treatment performance of wastewater samples (QCVN 14-MT:2015: Vietnam National technical regulation on domestic wastewater)

When conducting experiments with increasing concentration of H_2O_2 from 0,15.10^{-3} mol/L to 0,75.10^{-3} mol/L, as the value of COD decreases gradually, the treatment efficiency increases significantly and quickly reaches maximum at the concentration of $[H_2O_2]_0$ = 0,75.10^{-3} mol/L with the corresponding efficiency equals 80,89%, and the COD_{out} equals 195 mg/L. Continuing to add more H_2O_2 immediately increased COD again and reduces the treatment efficiency. The above change can be explained as follows: H_2O_2 participates in the intracellular structure of the catalytic complex $[Mn(EDTA)]^{2-}$ to form an active intermediate complex $[MnEDTAH_2O_2]^{2-}$ [2,5,6]:

$$[Mn(EDTA)]^{2-} + H_2O_2 \longrightarrow [MnEDTA(H_2O_2)]^{2+}$$

In addition, H_2O_2 is involved in the reaction during the bond-making and bond-breaking stages, providing

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OH • radical [2,7]. Therefore, the higher the concentration [H_2O_2], the more peroxo-active intermediate complexes [$MnEDTA(H_2O_2)]^{2-}$ were formed leading to increasing rate of the decomposition of organic matter in wastewater and increase efficiency reach maximum with [H_2O_2] = $0,75.10^{-3}$ mol/L. When the concentration of [H_2O_2] continues to increase passing the maximum efficiency of the reaction, the excessed H_2O_2 causes an adverse reaction with $K_2Cr_2O_7$ in the medium containing H_2SO_4 acid in the COD determination step, making the COD value significantly increased due to the loss of remaining $K_2Cr_2O_7$.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2O_2 \rightarrow Cr_2(SO_4)_3 + 3O_2 + K_2SO_4 + 7H_2O$$

Based on the obtained results, the optimal concentration value of H_2O_2 ($0,75.10^{-3}$ mol/L) was chosen to perform the next investigation experiment.

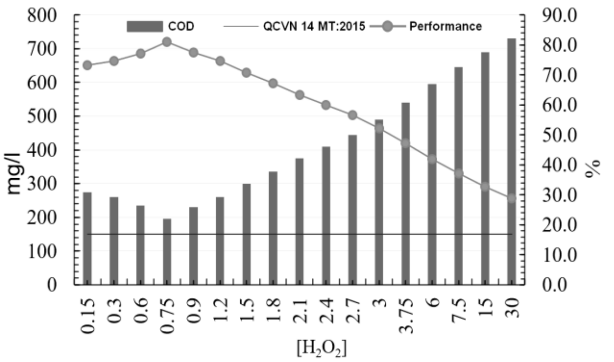

Figure 4: Effect of H_2O_2 concentration on COD treatment performance of wastewater samples (QCVN 14-MT:2015: Vietnam National technical regulation on domestic wastewater)

Effect of reaction time on processing efficiency

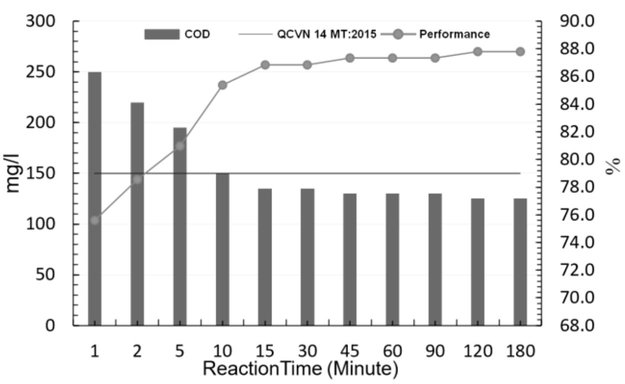

Figure 5: Effect of reaction time on COD treatment performance of wastewater samples (QCVN 14-MT:2015: Vietnam National technical regulation on domestic wastewater)

The experiment is conducted in the following conditions: pH = 10,5; $[Mn(EDTA)]^{2-}$ = 33,33 mol/L; $[H_2O_2]_0$ = $0,75.10^{-3}$ mol/L; reaction time changed from 5 ÷ 180 minutes. The analysis results of COD and treatment efficiency are presented in Figure 5.

According to the above experimental results, when the reaction time increases, the COD treatment efficiency increases significantly, especially the time from 0 ÷ 15 minutes. After only 15 minutes, the COD value was reduced to 135 mg/L, corresponding to an efficiency of 86,83%. But when the reaction time is greater than 15 minutes, the efficiency of the decomposition of organic pollutants in wastewater increases slightly.

This can be explained that the pollutant decomposition after 15 minutes has reached the final stage and reached its maximum value, so waiting for the longer time does not mean very much. And these experiments also show that with this treatment method, there are advantages in terms of time and reaction speed. The reaction time of 15 minutes then was chosen as the best optimal treatment time.

Conclusion

The results obtained through studying the influence of the factors β, pH, $[H_2O_2]_0$, $[Mn(EDTA)]^{2+}$ and reaction time on H_2O_2 decomposition in the system (II) indicate that the formation of complex forms catalyst $[Mn(EDTA)]^{2-}$ and are effective for the COD treatment. The catalytic activity of the complexes on the efficiency of treating persistent organic matter in the sample (COD) was evaluated. The optimal conditions for handling the sample with COD_{in} = 1025 mg/L (COD_{out} = 135 mg/L) were determined: β=1; $[H_2O_2]_0$ = $0,75.10^{-3}$ mol/L; $[Mn(EDTA)]^{2-}$ = 33,33 mol/L, pH=10,5; t = 15 minutes. The results meet Vietnam National technical regulation on domestic wastewater (column B: domestic wastewater discharged into receiving facilities not using for sources of domestic water supply) and it is promising for the potential to expand the scope of large-scale processing.

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