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Study on printing wastewater treatment by decomposition reaction H_2O_2 catalyzed of complex between ion Ni^{2+} and citric acid

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ABSTRACT

In this article, the results of the research on organic pollutant treatment in the wastewater of printing processes on fabric by H_2O_2 under the catalytic role of the complex between ion Ni^{2+} and Citric acid (H_4L) were presented. The condition of pH, H_4L/Ni^{2+}, H_2O_2, Ni^{2+} concentration has been explored to get the optimal conditions for improving COD efficient treatment. The results provide the solutions of the homogeneous complex catalysts in the industrial wastewater treatment at room temperature and atmosphere.

Introduction

The wastewater discharged from printing processes (on fabric, silk, papers, etc...) originated from craft villages and factories located in industrial zones often has a high COD concentration and color [1,2]. It shows that the waste water 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 ...

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 ($OH^\cdot$) - capable of oxidizing most persistent organic compounds [3,4,5,9]. 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. It is worthy to note that this is an improved method to expand the classic Fenton system in the environmental treatment processes [5].

In principle, the process of printing on fabric can be done by employing the method of screen printing or printing on automatic machines and lines. The ink is put on the molds, arranged in order and colors according to manufacturing operations. At the end of the process, the source of wastewater is mainly the printing frame washing water, printing knives, ink stirrers and some measuring devices and ink tanks. According to the survey, the current recovery of printing ink from the printing industry wastewater has not yet been an optimal process and has a wide range of usage, so most of the chemicals used still exist in the wastewater. Due to the potential environmental hazards, the COD treatment from fabric printing wastewater with the homogeneous catalyst complex of Ni^{2+} and citric acid (H_4L), activating H_2O_2 molecules was studied. The content of the paper focuses on evaluating the performance of the organic matter treatment in the sample through the COD indicator. The wastewater was collected after washing the printing mold of the printing process on the cotton fabric of Kim Hoang Printing One Member Company Limited. The studied printing ink is a specialized rubber ink used for fabric printing according to Oeko-Tex100 standard with the main components being Acrylic resin, Pigment color; does not contain Phthalate, Formaldehyde, heavy metals ...

In this paper, two research systems have been explored as follows:

Wastewater – Ni^{2+} - H_2O_2 (I)
Wastewater– H_4L- Ni^{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 were determined both before and after the treatments include: pH, COD according to TCVN 6491:1999 (ISO 6060:1989).

Results and discussion

It is clear that it is important to study the role of ion Ni^{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 (citric acid-H_4L).

Wastewater – Ni^{2+} - H_2O_2 (I)

Reaction's conditions: $[Ni^{2+}]_0$= 2.10^{-3}M; $[H_2O_2]_0$=1.10^{-2}M; COD_{in}= 3122 mg/L; pH=10.5; t=120 minutes...

The results of the studied system (I) show that the treated wastewater has a change in COD value (3120 mg/L) is not significantly different from the original COD (3122mg/L). In a relatively high pH environment, with large concentrations of $[Ni^{2+}]$ (~10^{-3}M), Ni^{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 terminating catalytic activities [6,7].

Consider the flowing system (II)

Wastewater– H_4L- Ni^{2+} - H_2O_2 (II)

The influence of pH on COD treatment's efficiency

Reaction's conditions: $[Ni^{2+}]_0$=$[H_4L]_0$= 2.10^{-3} (mol/L); $[H_2O_2]_0$= 1.10^{-2}(mol/L); COD_{in}= 3122 mg/L; t=120 minutes; t=30^0C

The reaction environment, pH, is a factor that has a great influence on the formation and existence of the complex that acts as a catalyst for the reaction process, especially in the case of the decomposition reaction H_2O_2, which is a very reactive reaction and sensitive to the reaction environment [5,7]. Therefore, it is necessary to study the effect of pH on the reaction rate or the efficiency of the treatment process. Experimental results are shown in Figure 1.

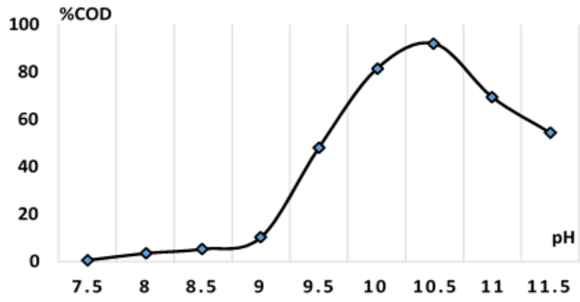

Figure 1: Effect of pH on COD treatment performance of wastewater samples

At pH <7.5, the capability of the COD treatment is very low. This can be explained as the ability of H_4L to dissociate into L^{4-} according to (II) is very weak, the ability of the catalysis complex to form a mono-nuclear complex $[NiL]^{2-}$ has a very small concentration or can be complex. The catalyst has not yet been formed, resulting in a very low or even not react at all in the H_2O_2 decomposition reaction.

At pH (7.5 ÷ 11): COD treatment efficiency increases and reaches the highest (92%) in the direction of increasing pH, which proves that the reaction rate increases due to H4L dissociation, the higher the pH, the more likely it is to create L^{4-} as much according to the principle of equilibrium shift:

$$H_4L \xrightarrow{-H^+} H_3L^- \xrightarrow{-H^+} H_2L^{-2} \xrightarrow{-H^+} HL^{-3} \xrightarrow{-H^+} L^{4-}$$

The greater the concentration of ligand $[L^{-4}]$, the higher the ability of Ni^{2+} and L^{4-} ions to form $Ni_2^{2+}L_2^{4-}$ complex with higher catalytic activity [4,6,8]. This leads to the increasing of the rate of H_2O_2 decomposition process to create free radicals [4].

Obtained results showed that at pH>10.5, COD treatment efficiency was reduced. At pH = 11, COD removal efficiency is 69.4%. It can be seen that, at the high pH, the hydrolysis occurs, causing complexes to convert to hydroxide and precipitate, causing the system to lose the homogeneity and reduce the activity of the catalytic complex. On the other hand, other studies showed that at high pH (> 11) H_2O_2 itself decomposes into H_2O and O_2.

The influence of transition metal ligan concentration ratio on COD treatment's efficiency

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Reaction's conditions: $\beta=[H_4L]_0/[Ni^{2+}]_0$; $[Co^{2+}]_0$ = 2.10^{-3} (mol/L); pH=10.5; $[H_2O_2]_0$= 1.10^{-2} (mol/L); COD_{in}=3122 (mg/L); t=120 minutes; t= 30^{0}C.

To qualitatively investigate the formation, the effect of the catalyst complex in COD treatment as well as determine the optimal ratio between metal ion concentration and ligan, quantity β =$[H_4L]_0/[Ni^{2+}]_0$ (ratio between ligand concentration and metal ion concentration) is established.

The results show that with β = 0: The system becomes (I) system, almost no catalytic complex formation due to the hydrolysis of Ni^{2+} ions at pH = 10.5.

With β > 0. Organic matter existing in the wastewater begins to undergo the action of free radicals generated by the H_2O_2 decomposition process. Under the effect of ligand (H_4L), Ni^{2+} ions begin to gradually participate in the complexing process to form the catalyst.

Complex forming process tend to form highly reactive catalysts. The resulting complex causes the concentration of free Ni^{2+} ions in the solution to decrease along with the increasing of the concentration of $[H_4L]_0$, limiting the hydrolysis of Ni^{2+} ions, changing oxidation-reducing potential, changing the mechanism of the hydroxyl radical($^{\cdot}$OH) generation. The value of β was set at the value 0.5; 0.75; first; 1.5; 2; 2.5; 3, then at β = 1 the processing efficiency% COD is the largest, 91.8%. This proves that the concentration of the catalyst complexes also reaches the maximum at β = 1. Thus, the rate of decomposition reaction is inversely proportional to β while propotional to the concentration $[H_4L]$ 0. This result can be explained in the following respect:

According to [6] at pH = 10.5, the ratio $[L^{4-}]$ /$[H_4L]_0$ = 10^{18}. This result has shown that: under the current conditions, H_4L has dissociated completely into L^{4-} form. Thus when β = 1 or $[H_4L]_0$ / $[Ni^{2+}]_0$ = 1 can be considered as $[L^{-4}]$/ $[Ni^{2+}]_0$ = 1, the resulting catalytic complex can be a bi-nuclear complex because during the dime process a mono-nuclear complex has with very high catalytic activity:

$$Ni^{2+} + L^{4-} \leftrightarrow NiL^{2-}$$
$$2NiL^{2-} \leftrightarrow Ni_2L_2^{4-}$$

However, with a value of β>1, COD efficiency decreases. The cause may be due to excess H_4L. At that time, H_4L acts as a competitive agent of the group $^{\cdot}$OH with H_2O_2 reduces the rate of H_2O_2 decomposition reaction, thereby reducing COD treatment efficiency.

In summary, the presence of H_4L ligand with different values of β can create two types of catalyst complexes. It is a dual-core compound $[Ni_2L_2]^{4-}$ and a single-core compound $[NiL]^{2-}$. Experiments show that the dual-core complex is more active. When changing the value of β in the upward direction, the equilibrium will shift toward the direction of creating many ligand complexes with reduced catalytic activities. In the following influence studies, β = 1 was selected as the optimal value.

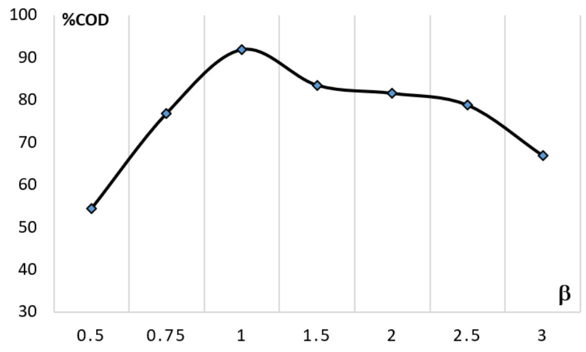

Figure 2: Effect of β on COD treatment performance of wastewater samples

The influence of Ni^{2+} transition metal ion concentration on COD treatment's efficiency

Reaction's conditions: β=1; $[H_2O_2]_0$= 1.10^{-2} (mol/L); COD_{in}=3122(mg/L); pH=10.5; t=120 minutes; T=30^{0}C

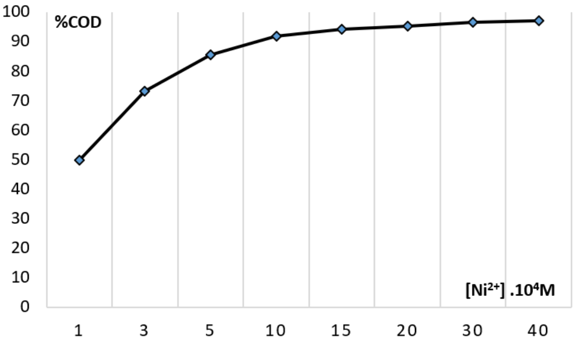

Figure 3: Effect of $[Ni^{2+}]_0$ on COD treatment performance of wastewater samples

The influence of Ni^{2+} ion concentration on the COD treatment performance is shown in Figure 3. We see that when $[Ni^{2+}]_0$ increases, COD treatment efficiency increases significantly. With the value of β = 1, keeping the other conditions fixed, when $[Ni^{2+}]_0$ increases, the complex between Ni^{2+} and L^{4-} emerges, increasing the concentration of the catalyst complexes. This result also confirms that the complex of ion Ni^{2+} has played a catalytic role.

According to [6] when $[Ni^{2+}]_0$ <1.10^{-3}(mol/L), the resulting catalyst complex is a mono-nuclear complex between Ni^{2+} and L^{4-}. When the concentration of $[Ni^{2+}]_0$ ≥ 2.10^{-3}(mol/L) appears, the bi-nuclear complexes

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between Ni^{2+} and L^{-4} make the catalytic activity increase, which means the increase of free radical formation. This can be explained as follows: When $[Ni^{2+}]_0$ is high, the possibility of collision and contacting between Ni^{2+} and L^{4-} is high, increasing the ability to create double cores between metal ions and ligand. At $[Ni^{2+}]_0 = 2.10^{-3} \div 4.10^{-3}$(mol/L) COD value <100 (mg/L) meets column B standards of national technical regulations QCVN 40: 2011 / BTNMT for the industrial wastewater.

The results of $[Ni^{2+}]_0$, β, pH effects on the decomposition of H_2O_2 in the (II) system above showed that the observed results are very compatible with each other in proving the creation into the one-nuclear catalytic complex $[NiL]^{2-}$ and the bi-nuclear $[Ni_2L_2]^{4-}$. In which, the catalytic activity of these complexes increases in order: $[NiL]^{2-} < [Ni_2L_2]^{4-}$.

The influence of $[H_2O_2]$ on COD treatment efficiency

Reaction's conditions: β=1; $[Ni^{2+}]_0$= $[H_4L]_0$= 2.10^{-3}M; COD_{in} = 3122 mg/L; pH=10.5; t=120 minutes; T=30^0C.

With the results obtained in the previous sections, the effect of $[H_2O_2]_0$ on the COD treatment performance continues to be studied in order to optimize treatment conditions. The results presented in Figure 4 show the decomposition reaction rate, processing efficiency increases proportional to the concentration increase $[H_2O_2]_0$. At concentrations less than 10^{-2}(mol/L), the H_2O_2 molecule enters the intracellular complexes in the form of $[Ni^{2+} LH_2O_2]$. This is a formation of active intermediate complex and at a certain limit when increasing the concentration $[H_2O_2]_0$, the rate of H_2O_2 decomposition process will increase or in other words, the effectiveness of treating difficult-decomposing organic matter that exists in the sample will increase.

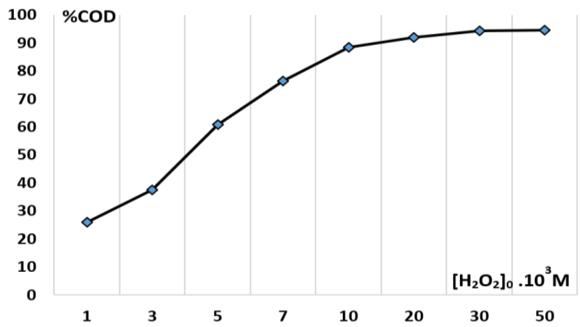

Figure 4: Effect of $[H_2O_2]_0$ on COD treatment performance of wastewater samples

$$[Ni_2L_2]^{4-} + 2H_2O_2 \rightleftarrows [Ni_2L_2(H_2O_2)_2] \longrightarrow [Ni_2L]^{2-} + 2OH^- + 2\,{}^*OH$$

At a concentration of ≥ 1.10^{-2}(mol/L), it is possible that the active intermediate complex formed will have the form $[Ni^{2+}L(H_2O_2)_2]^{4-}$ so the treatment effect is more effective.

However, some experimental results show that the possibility of excess H_2O_2 will cause oxidation reaction of citric acid (H_4L) at high pH, thereby reducing the stable concentration of the catalyst complex, reducing treatment efficiency, and increase the cost of wastewater treatment.

$$[NiL]^{2-} + H_2O_2 \rightleftarrows [NiLH_2O_2]^{2-} \longrightarrow [NiL]^- + OH^- + {}^*OH$$

Conclusion

The results obtained by determining the influence of the factors $[Ni^{2+}]_0$, β, pH and $[H_2O_2]_0$ on H_2O_2 decomposition in the system (II) above indicate that the formation of complex forms catalyst $[NiL]^{2-}$ and bi-nuclear $[Ni_2L_2]^{4-}$ are effective for the COD treatment. The catalytic activity of the complexes on the efficiency of treating persistent organic matter in the sample (COD) increases in the following order: $[NiL]^{2-} < [Ni_2L_2]^{4-}$. The optimal conditions for handling the sample with COD = 3122 mg/L were determined: : β=1; $[Ni^{2+}]_0$= $[H_4L]_0$= 2.10^{-3}(mol/L); $[H_2O_2]_0 = 3.10^{-2}$ (mol/L); pH=10.5; t = 120 minutes; t=30^0C have been established, it is promising for the potential to expand the scope of large-scale processing. In addition, the research results will contribute to improving the environmental protection, promoting sustainable production at Kim Hoang Printing Co., Ltd. in particular and printing facilities on fabric in other companies in Vietnam.

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