Fenton/ozone-based oxidation and coagulation processes for removing metals (Cu, Ni)-EDTA from plating wastewater

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ABSTRACT

Wastewater containing heavy metals has caused many serious problems to land and marine environments. These heavy metal-laden wastewaters containing organic complexing agents are the consequence of using large-scale industrial applications for dissolving metals. Ethylenediaminetetraacetate (EDTA) is a widely used complexing agent in plating, metal finishing and chemical cleaning industries. However, due to the dramatic increase in the solubility of metal ions, EDTA has negative impact on heavy metals removed in wastewaters by conventional precipitation processes. This study aims to find the optimal conditions of combined/hybrid process of advanced oxidation and coagulation to treat metals-EDTA containing Cu, Ni plating wastewater from an electroplating manufacturer in Vietnam. The effects of pH, H_2O_2 dose, Fe^{2+} dose, ozone, reaction time and poly acrylic acid (PAA) dose were investigated. Results indicated that the 3-stage treatment process at the optimal conditions could remove 99.7 % of Ni and 99.72 % of Cu. The effluent of wastewater after the whole treatment process met the Vietnamese national regulation on industrial wastewater (QCVN 40:2011/BTNMT) for NH_4^+, Cu and Ni at column A and COD at column B. In short, the combined advanced oxidation processes and coagulation/floc-culation could successfully be applied for plating wastewater treatment.

1. Introduction

The global water sources have been severely polluted by heavy metal ions, and organic compounds, which are generated daily from industrial, agricultural, traffic and residential activities [1]. Specifically, heavy metal ions in wastewater produced from metal smelting, electrolysis, electroplating and other industrial activities cannot be degraded using microorganisms and consequently they contaminate the soil, water and air. Many techniques (adsorption, photocatalyst, precipitation, coagulation, flocculation, etc.) have been successfully developed for removing these heavy metals from water and wastewater. Nevertheless, the co-existence of complexing agents (ethylenediaminetetraacetate, pesticides, fertilizers, detergents, plasticizers, pharmaceuticals, oils, etc.) make the composition of heavy metal containing wastewater more complicated [1]. Ethylenediaminetetraacetate (EDTA) is a widely used complexing agent in plating, metal finishing and chemical cleaning industries. Heavy metals can easily form stable metal complexes with varying structures and levels of toxicity [2,15]. The formation of toxic

metal organ ligands of metals and EDTA results in a difficulty in removing heavy metals from wastewater when using various conventional precipitation processes. This is due to the dramatic increase in the solubility of metal ions.

Over the last few decades, advanced oxidation processes (AOPs) have been developed for oxidizing many organic compounds into inorganic forms. Amongst these studied AOPs, the Fenton process has proved its efficiency for the abatement of toxic pollutants in electroplating industrial effluents [3]. Alternatively, hydroxyl radicals can be highly reactive, not selective, easily generated, powerful oxidants, short-lived, harmless, and control the rate of reaction [1].

In Fenton reaction, hydroxyl radicals generated from a mixed solution of ferrous ions and H_2O_2, have strong oxidizing properties, which can efficiently oxidize many organic-metals compounds into inorganic forms [1,16]. However, the sole application of Fenton reaction does in fact suffer from poor oxidation efficiency due to the complexity and recalcitrant nature of the reaction byproducts [3]. Recently, studies on improving the integrated system for better removal efficiency of

potential toxic organic pollutants to meet the wastewater discharge standards have attracted much interest. Ozonation and its combining techniques, e.g., O_3/H_2O_2, O_3/Fe^{2+} and $O_3/Fe^{2+}/H_2O_2$ have proved their effectiveness in the destruction of non-biodegradable toxic contaminants through two mechanisms: direct reaction ($E_0 = 2.08$ V); and hydroxyl radical induced oxidation ($E_0 = 2.80$ V) (Zhao et al., 2017). Therefore, the combined employment of Fenton and ozone-based AOPs is indeed a potential approach for the removal of metal-complexes in electroplating wastewater, which achieves the advantage of complementarity. Fenton is more effective for de-complexation while ozone is more effective for mineralization. Thus, Fenton process is applied for de-complexing the EDTA-metal complexes and decomposing of more stable organic compounds. Then ozone helps to degrade the remaining and weaker compounds. Furthermore, in previous studies the target wastewater contained only a single metal (Zhao et al., 2017; [3,4]). A study to investigate the removal efficiencies of multi-complex of EDTA-metals, optimal conditions, mechanisms of chelates degradation and intermediates of treatment process is crucial.

In the present work, two selected target pollutants are Cu and Ni, which are representative pollutants in electroplating effluents from an electroplating company in Vietnam. Firstly, factors affecting the Fenton/ozone as well as coagulation/flocculation processes (e.g. such as, H_2O_2 dosage, pH, O_3 dosage, Fe^{2+} dosage, flocculants dosage and order of reactions) were investigated to ascertain the best conditions for abating of Cu and Ni from plating wastewater. Subsequently, other water parameters were also analyzed including COD, NH_4^+ and NO_3^- to evaluate treatment efficiency. Finally, the removal mechanism of heavy metals was proposed and discussed towards a better understanding and improvement of AOPs processes.

2. Materials and methods

2.1. Materials

The materials and chemicals used in this study include: $FeSO_4.7H_2O$ (99 %); H_2O_2 solution (30 %); and Poly acrylic acid (PAA) solution 0.1 % solution prepared from commercial PAA powder (anionic flocculants commercially named A400).

- Ozone generator Z-2 Cuongthinh Technology., JSC. (capacity of the ozone generator 2 g per hour).
- Real plating wastewater was taken from an electroplating in Bac Ninh province, Vietnam. Plating wastewater was taken from a company in Bac Ninh province and the following quality parameters were required: Cu: 100–301 mg/L; Ni: 44–51 mg/L; COD: 2520–4000; NO_3^-: 1.2–3.5 mg/L and NH_4^+: 31–102 mg/L.
- A synthetic wastewater sample containing suitable amounts of EDTA, Cu, Ni and NH_4^+ was prepared to compare the efficiency with the real electroplating wastewater.

2.2. Methods

2.2.1. Fenton/ozone reaction and coagulation process design

The Fenton/ozone-based oxidation and coagulation process experimental set-up is shown in Fig.1. A volume of real plating wastewater was placed into a 2 - liter beaker and wastewater was treated following the 3 – stage procedure: (1) coagulation/flocculation: adjusting pH values, where the suitable amounts of chemicals were added; the mixture was stirred, then rapidly settled and filtered; (2) adjusting pH values; the effluent and amounts of Fe^{2+} solution and H_2O_2 were put together, and then stirred at 100 cycles per min for a certain time. The mixture was then aerated with ozone for another specific time; and (3) lastly, the solution pH was adjusted and PAA was supplied, stirred, flocs were settled and filtered. The effluent was filtered through a 0.45 μm filter paper, and concentrations of Cu and Ni were analyzed by Atomic Absorption Spectrometer AA6800, Shimadzu at Faculty of Environmental Sciences, University of Science, Vietnam National University, Hanoi. Other parameters such as COD, NH_4^+, NO_3^- were measured using analytical standard methods.

2.2.2. Factors affecting the performance of the Fenton/ozone process

The relevant factors include H_2O_2 dosage, Fe^{2+} dosage, Fenton effluent pH, O_3 dosage and reaction time to assess the efficiency in removing heavy metals via the Fenton/ozone process. The details are described below:

- Effects of H_2O_2 dosage were examined. 1 L of real plating wastewater was placed into a 2-L reactor. Then 1200 mg of Fe^{2+} (taken from $FeSO_4.7H_2O$ powder) was added. Solution pH was not adjusted.
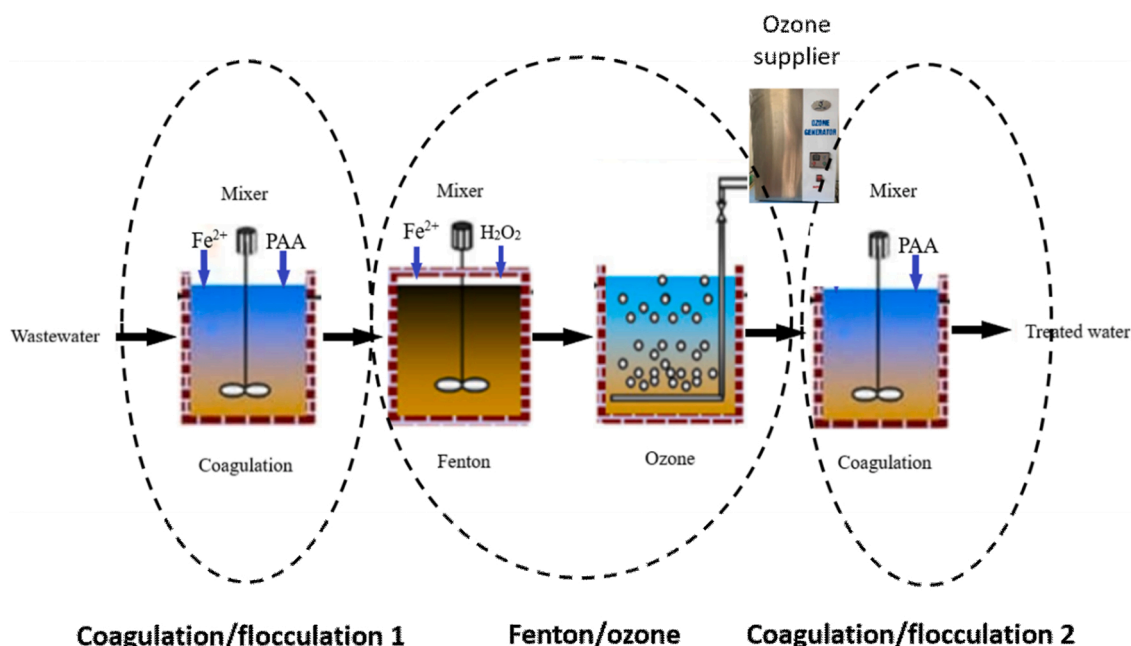

Fig. 1. Fenton/Ozone-based oxidation and coagulation process experimental set-up.

_M._Subsequently, different volumes of H_2O_2 30 % solution (0; 5; 10; 20; 25 and 30 mL) were added. The mixtures were stirred for 10 min, then ozonation occurred for 40 min. The effluents were filtered through a 0.45 μm filter paper and parameters (Cu, Ni, COD, NH_4^+, NO_3^-) were measured.

-To document the effects of Fe^{2+} dosage, amounts of Fe^{2+} solution (150; 250; 300; 500; 600; 700; 800; 900; 1200; 1500; 1800 mg Fe) were put into wastewater. This was followed up by using the most suitable dosage of H_2O_2 solution obtained from the previous experiment being added. Solution pH was not adjusted. Next, the subsequent steps were carried out as per the same procedure according to the H_2O_2 dosage influence tests.

- For investigating the effects of Fenton solution pH on the removal efficiency of Fenton/ozone reaction, the most suitable dosages of H_2O_2; Fe^{2+} solutions were prepared. The Fenton solution pH being adjusted to 3, 4, 5, 6, 7, and 8. Subsequent steps were carried out as the same procedure as according to the H_2O_2 dosage influence tests.
- Effects of O_3 dosage to the AOPs of plating wastewater were observed. The most suitable conditions: dosages of H_2O_2; Fe^{2+}, pH were prepared. The mixture was stirred for 10 min. Specific amounts of ozone (dose of 40; 83; 125; 166; 208; 250; 833.5 mg/L) were aerated in the mixture for 40 min. Subsequent steps were carried out as the same procedure as per according to the H_2O_2 dosage influence tests.
- Effects of reaction time were studied in terms of the most suitable conditions such as dosages of H_2O_2, Fe^{2+}, solution pH. The mixture was stirred for various amounts of time (2, 5, 10 and 20 min). The most suitable dose of ozone was aerated at different amounts of time (10, 20, 30, 40, 50 and 60 min). Subsequent steps were carried out as the same procedure as done in the previous tests.

2.2.3. Factors affecting the coagulation/flocculation process

Factors such as dose of Fe^{2+} and PAA and pH regarding the coagulation and flocculation process were explored. The details are described below:

- For examining the effects of Fe^{2+} and PAA doses to coagulation/flocculation process, amounts of Fe^{2+} and PAA solution (0.2, 0.5, 0.8, 1, and 2 mL) were added after the Fenton/ozone process to implement coagulation/flocculation. The sizes and shapes of flocs and settling efficiencies were inspected during the experiments. Subsequent steps were carried out in the same way as the previous tests in Section 2.2.2.
- Effects of pH on efficiency of coagulation/flocculation practices were explored. Various pH values (7, 8, 9, 10, and 11) were used for the experiments. The size and shapes of flocs and settling efficiencies were inspected during the experiments. Subsequent steps were carried out in the same way as the previous tests in Section 2.2.2.

2.2.4. Testing the removal efficiencies with the synthesized wastewater using the Fenton/ozone reaction process

The same procedure to treat the real plating wastewater was applied for toxicants abatement from synthesized wastewater, which was prepared in Section 2.1. A liter of synthetic wastewater, various dosages of Fe^{2+}, H_2O_2, Fenton solution pH value, O_3, Fe^{2+}, PAA and coagulation/flocculation solution pH value served to compare the removal efficiencies with the treatment of real plating wastewater.

2.2.5. Changes in oxidation–redox potential (ORP) during the Fenton/ozone and coagulation/flocculation processes

The changes in oxidation–redox potential (ORP) during the Fenton/ozone process were observed in order to understand the reaction and to better calculate the optimal amounts of reagents and duration of the Fenton/ozone process. An ORP hand-held equipment known as Hanna HI 991003 was used for observation during the test in various stages of the Fenton/ozone and coagulation/flocculation processes. The AOPs

were carried out following the 3-stage processes of Fenton, ozone and coagulation/flocculation as Fig. 1 at the optimal conditions (achieved from Sections 2.2.2 and 2.2.3). Changes in the ORP values of the mixture were monitored during the treatment process at certain times to include the influent wastewater, after coagulation and flocculation 1, after Fenton, after ozone, after coagulation and flocculation 2.

2.2.6. Analysis of heavy metals, other water quality parameters, oxidation reduction potential (ORP)

Concentrations of Cu and Ni in the samples were measured using Atomic Absorption Spectrometer AA6800, Shimadzu. Other water quality parameters, namely COD, NH_4^+, NO_3^- were also measured following analytical standard methods TCVN 6491:1999, TCVN 6180:1996/ISO 7890-3:1988(E), TCVN 6179-1:1996/ISO 7150-1:1984 (E) and using UH5300 UV–vis, Hitachi, Japan. Oxidation Reduction Potential (ORP) in the Fenton/ozone solution was measured using the previously mentioned Hanna HI 991003 equipment.

Treated wastewater samples at different stages of coagulation/flocculation: Fenton; ozone and coagulation/flocculation processes were analyzed using HPLC Shimazu LC-20A equipped with ODS C18 HPLC Column, detector UV/VIS SPD-20A at a wave length of 210 nm; and utilized mobile phase was (A) acetonitrile and phosphoric acid (v/v) 99.9:0.1 and (B) de-ionized water and phosphoric acid (v/v) 99.9:0.1 at the ratio: 50 % A and 50 % B. Intermediates of the treatment process (after Fenton reaction and after ozone reaction) were analyzed using GC–MS 6890/5973i, Agilent, equipped with column DB-5MS 30 m, 0.25 mm I.D, 0.25 μm. Temperature program: 50 (hole in 5 min), increased at the rate of 5 °C/min to 100 °C (hold in 1 min), then increased at the rate of 10 °C/min to 250 °C (hold in 5 min). The samples were prepared following the steps: (1) the solution was extracted using ethyl acetate several times (5 mL each time) while using Na_2SO_4 to remove water, collecting the extracting solution and concentrating to near-dry in a rotary evaporator at 40 °C; then adding 1 mL of ethyl acetate to the solution and transferring to 1.5 mL vial dried by pure nitrogen gas; (2) subsequently, 20 μL pyridine, 400 μL dioxane, and 100 μL silane reagent (N,O-bis(Trimethylsilyl)trifluoroacetamide : Trimethylchlorosilane mixture, v/v = 99:1) were added to the above sample vial; (3) finally, the mixture was Voltex shaken in 30 s and derivatized for 20 min at 60 °C.

All samples in this study were analyzed in duplicate and mean values were presented. Data processing was completed with Microsoft Excel 2016, whereas diagramming and correlation analysis were done with Origin Pro 2016.

3. Results and discussion

3.1. Performance optimization of Fenton/ozone oxidation treatment

3.1.1. Effects of H_2O_2 dosage in the Fenton/ozone process

The effects of H_2O_2 dosage on the metal concentration in the effluent are illustrated in Fig. 2. When the dose of H_2O_2 rose from 1 to 20 mL/L, the higher dose of H_2O_2 resulted in better removal efficiencies from 62.63 to 99.55% for Cu, and 63.86 to 99.48% for Ni, respectively. These removal efficiencies reached equilibrium at a dose of 20 mL/L. Subsequently, the rise from 20 to 25 mL/L of the dose did not result in notable changes of removal performance for both Cu (99.76 %) and Ni (99.27 %). Hence, the selected dosage of H_2O_2 for further experiments was 20 mL/L. According to theoretical and practical studies, the dosage of the Fenton reagents is calculated with reference to the COD concentration of the influent of Fenton treatment. Concisely, the mole number of the desired H_2O_2 was calculated by the mole ratio of the H_2O_2 mole to COD mole (0.5:1 to 1:1) [5]. However, the actual dosages of the Fenton reagents not only depend on the concentrations of COD, but also heavy metals and other substances. The experimental results indicated that the mole number of consumed H_2O_2 in this study was:
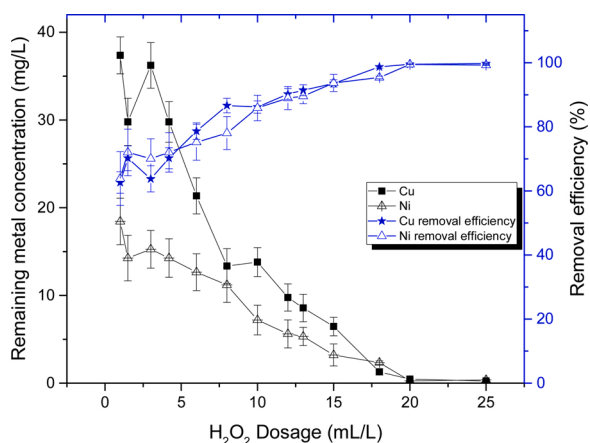
Fig. 2. Effects of H_2O_2 dosage on the metal removal efficiency of the Fenton/ozone effluent.

$$\frac{Volume(mL) * density(g/mL) * percentage(\%)}{Molecular weight} = \frac{20 * 1.45 * 30}{34 * 100} = 0.256 mol$$

The molar ratio of H_2O_2 to COD in this study was 0.256:(4000/(1000*32)) = 0.256:0.125 = 1:2. This molar ratio was higher than the research conducted on perylene pigment wastewater treatment by Fenton-enhanced biological processes (1:1) [5]. This could be explained by the Fenton/ozone process, which is not selective, thus the target pollutants of the reaction include all pollutants, such as heavy metals, organic matter, ions, and other substances [1].

3.1.2. Effects of Fe^{2+} addition in the Fenton/ozone process

In the Fenton reaction, the molar number of required Fe^{2+} mass was calculated by the mass ratio of the mass of Fe^{2+} to the mass of H_2O_2 (0.3:10 to 1:10) [5,6]. Fig. 3 shows the experimental results of the Fe^{2+} dosage in the Fenton proces. Based on the dose ranging from 150 to 1200 mg/L, the increase in Fe^{2+} dosage led to better removal efficiency (56.8–98.39% for Cu and 64.12–97.02% for Ni). Nevertheless, when the dose increased to 1500 and 1800 mg/L this resulted in a slight decline in the removal efficiencies (96.13 % for Cu and 95.41 % for Ni at Fe^{2+} dose of 1800 mg/L). This could be explained by the redundancy of Fe^{2+} in affecting the Fenton/ozone process. As an amount of Fe^{2+} which was added to the coagulation/flocculation process, it appears that a part of this amount could still have existed in the solution. Furthermore, the exuberance of Fe^{2+} could possibly lead to chemical waste and in turn the increase in COD concentration. Thus, the dosage of Fe^{2+} in the
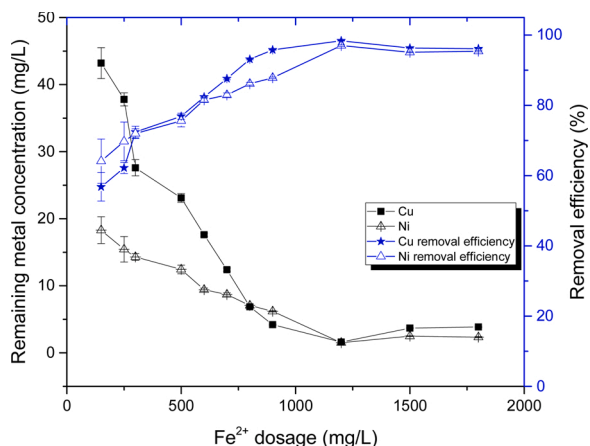
Fenton/ozone process chosen was 1200 mg/L. The observed best ratio of mole number of Fe^{2+} to mole number of H_2O_2 in this study was: (1200/56):0.256 = 1:12. This outcome agreed with theoretical and previous studies with mole number of Fe^{2+}: mole number of H_2O_2 in the 0.3:10 to 1:10 range [5,6].

3.1.3. Effects of effluent pH on the removal of heavy metals using the Fenton/ozone process

The effects of Fenton solution pH values (between 2 and 11) on the removal efficiencies of heavy metals when employing the Fenton/ozone reaction process are described in Fig. 4. These outcomes illustrated that pH values have great impacts on the removal of heavy metals through the Fenton/ozone reaction. Based on the results in Fig. 6, optimal pH values for the removal of heavy metals were 3 and 6. Both lower and higher pH values caused declines in removal efficiencies. Predominantly, the subsequent step after Fenton reaction was to combine the Fenton and ozone processes after the introduction of Fe^{2+} and H_2O_2. Many investigators claimed that the most suitable pH values for Fenton oxidation were around 3, notwithstanding any objective impurities [3,7, [12]. On the other hand, during the ozonation process, the indirect reactions of hydroxyl radicals under neutral and high pH values are more efficient than the direct reactions of ozone molecules in acidic conditions [3,8]. This might explain why there were two different optimal pH values for combining the Fenton and ozonation processes. These explanations confirmed the experimental results that treatment performance was efficient when first separating the Fenton reaction and then continuing with the Fenton/ozone reaction. The same conclusion was also achieved by Zhao et al. [3] for the removal of Ni-EDTA by Fenton and ozone-based oxidation processes.

3.1.4. Effects of O_3 dosage

The impacts of O_3 dosage on the removal performance of Cu and Ni by Fenton/ozone process are depicted in Fig. 5. Removal efficiencies of Cu and Ni improved from 80.3 to 98% and 67.9 to 81%, respectively, when the O_3 dose rose from 40 to 125 mg/L. When the dosage of O_3 increased to 166 mg/L, the efficiency in removing Ni increased to 98.68 while removal efficiency of Cu was 98.46 %. According to previous studies, larger doses of O_3 will achieve a stronger driving force for the gaseous liquid mass transfer, supporting the reaction to fully proceed with H_2O_2 and Fe^{2+} [9,10] The doses of O_3, which were above 166 mg/L, did not lead to any significant improvement in metal abatement performance. Consequently, the optimal dose of O_3 chosen from these experiments was 166 mg/L.

The experimental results revealed that the most suitable conditions for the Fenton/ozone oxidation treatment were 1200 mg/L Fe (FeSO$_4$.7H$_2$O) +20 mL/L H_2O_2, stirring for 10 min, ozone aeration/

Fig. 3. Effects of Fe^{2+} dosage on the metal removal efficiency of the Fenton/ozone effluent.
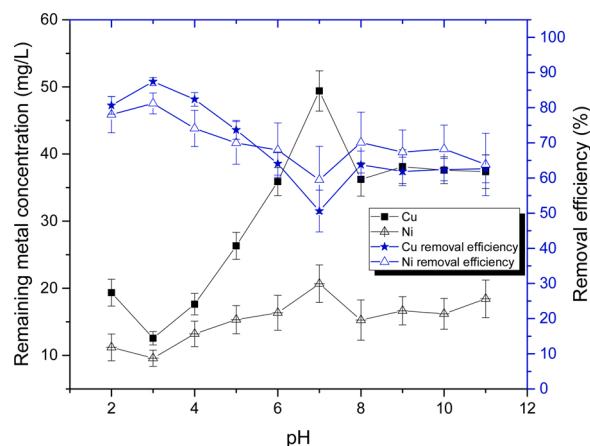

Fig. 4. Effects of pH on the metal removal efficiency of the Fenton/ozone effluent.
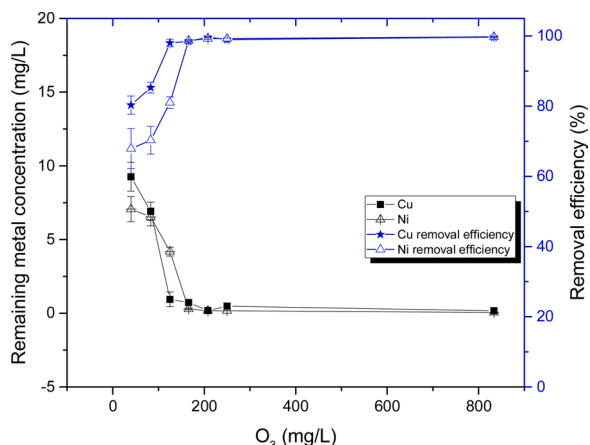
Fig. 5. Effects of O_3 dosage on the metal removal efficiency of the Fenton/ozone effluent.

ozonation in 20 min, adjusted pH level 6–8 and then continuous ozone aeration/ozonation in 25 min (the result obtained from experiments in Section 2.2.2 regarding effects of reaction time, data is not shown).

3.2. Performance optimization of coagulation/flocculation process (physico-chemical 1 and 2)

3.2.1. Effects of pH

Documented results regarding pH affecting the coagulation/flocculation process's removal of heavy metals are presented in Fig. 6. Solution pH has great impacts on the efficiency of the coagulation/flocculation 2 process. Abatement efficacy of Cu achieved the best values from pH 8 to above while from pH 10 to above most of the Ni was removed. Due to the existence of both Cu and Ni in the real plating wastewater in this study, pH 10 was chosen as the most appropriate pH value for conducting the coagulation/flocculation process. The reported optimal pH values for different kinds of metals were as follows: Ni: 10.5–11; Cu: 8–8.2; Al:11; Cr:8.5–9; Fe^{3+}:3−4; Fe^{2+}:8−9; Pb:9−10; Zn:9−10; Ag:12; Cd:9−11 [11].

3.2.2. Effects of Fe^{2+} dosage

In the coagulation/flocculation process 1, an amount of Fe^{2+} was added to the wastewater samples as coagulant. To elucidate the effects of Fe^{2+} dosage on removal efficiency of heavy metals through this

process, various doses of Fe^{2+} were applied:500;1000;1200; and 1500 mg/L. The experimental results in Fig. 7 indicated that removal efficiencies of Cu and Ni (84.3 and 49.8 %, respectively) were best reached at a dose of Fe^{2+} 1200 mg/L. Hence, a dose of 1200 mg/L Fe^{2+} was selected for the following experiments. Furthermore, the progress made in removing Cu proved to be more efficient than for Ni. This might be due to the stability constant of Ni complex being of higher value than Cu.

3.2.3. Doses of PAA in the physico-chemical 1 and 2

The doses of PAA solution were determined by observing the formation of macro flocs during the coagulation and flocculation process. Experimental results indicated that the amount of PAA solution for the process below is as follows: coagulation and flocculation in physico-chemical 1: PAA 2.4 mL, coagulation, and flocculation in physico-chemical 2: PAA 3.2 mL. The observation showed that treated wastewater after the coagulation and flocculation processes was much cleaner than the untreated wastewater.

3.3. Other water quality parameters

Table 1 displayed the removal efficiencies of other water quality parameters by the treatment process, including coagulation/

Fig. 7. Effects of Fe^{2+} dosage on removal efficiency in the coagulation/flocculation process 1.
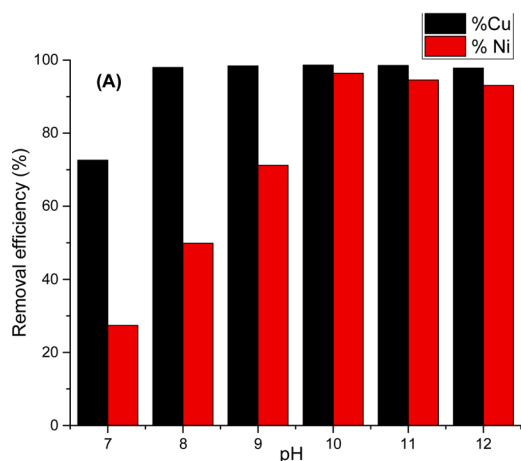

Fig. 6. Effects of pH on removal efficiency on the coagulation/flocculation process (A) and metal hydroxide precipitation chart (B - adapted from Hoffland Environmental, 2020)).
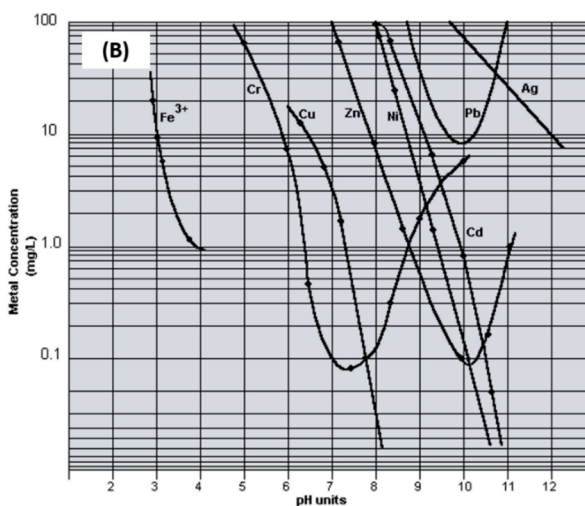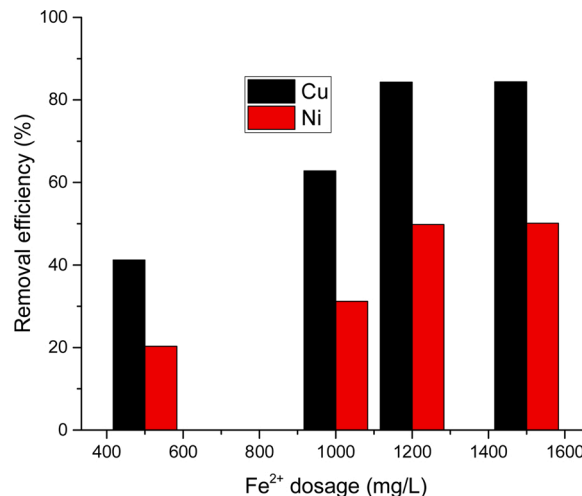
Table 1

Water quality parameters removal efficiencies at various stages of plating wastewater treatment processes.

Treatment process		COD (mg/L)	Removed COD (%)	NH_4^+ (mg/L)	Removed NH_4^+ (%)	NO_3^- (mg/L)	Removed NO_3^- (%)	Cu (mg/L)	Removed Cu (%)	Ni (mg/L)	Removed Ni (%)
Plating wastewater		4000	0	102	0	3.5	0	301	0	51	0
Coagulation and flocculation 1		1280	68	85.16	16.5	0.82	76.5	47.3	84.3	25.8	49.4
Fenton		720	82	21.55	78.8	2.94	16	15.6	94.8	13.9	72.7
Ozone		240	94	3.06	97	1.26	64	8.6	97.1	9.35	81.6
Coagulation and flocculation 2		140	96.5	2.42	97.6	1.2	65.7	0.84	99.7	0.15	99.7
QCVN 40/2011- BTNMT	Column A	75	–	5	–	No regulation	–	2	–	0.2	–
	Column B	150	–	10	–	No regulation	–	2	–	0.5	–

flocculation; Fenton; Ozone; Coagulation/flocculation. These processes are compared to the Vietnamese national technical regulations issued by the Ministry of Natural Resources and Environment (QCVN 40/2011-BTNMT). From the results documented in Table 1, coagulation and flocculation 1 can remove the following: 68 % COD; 16.5 % NH_4^+; 84 % Cu and 52 % Ni. Consequently, the utilization of coagulation/flocculation 1 in the first stage is essential for easily removing a large amount of contaminants such as free ions, and unstable complexes in order to prepare for the next stage of the Fenton/ozone process. Since Fenton/ozone is not a selective process, this kind of treatment would help to reduce the amounts of chemicals consumed [1,13]. As expected, the Fenton/ozone method is the main process employed to remove and degrade the contaminants, which cannot be abated by coagulation/flocculation 1 above. After the Fenton/ozone process, water quality parameters were COD 240 mg/L, NH_4^+ 3.06 mg/L, Cu 8.6 mg/L and Ni 9.35 mg/L. The moderately high concentrations of Cu and Ni measured after the advanced oxidation process could be explained by the existence of free Cu^{2+} and Ni^{2+} or the unstable complexes of Cu and Ni. This was demonstrated by the removal efficiencies during the coagulation/flocculation 2 in order to abate all the contaminants. This was done by increasing the pH and adding flocculants (PAA). Concentrations of COD, NH_4^+, NO_3^-, Cu and Ni after the whole treatment process were 140; 2.42; 1.2; 0.84; and 0.15 mg/L, respectively. In comparison to the Vietnamese national technical regulations, the treatment process does meet the regulation (QCVN 40:2011/BTNMT) for NH_4^+, Cu and Ni at column A and COD at column B [14].

The experimental results indicated that at the first stage the increase of pH supported precipitation and coagulation/flocculation processes and led to significantly reduction of metals (84.3 % Cu and 49.4 % Ni) and chemical oxygen demand (COD) of wastewater (68 %) (Table 1). If these amounts were not removed, they would have led to large consumptions of Fe and H_2O_2 in the Fenton/Ozone processes and a decrease in the efficiency of EDTA-Cu and EDTA-Ni chelates de-complexation process. Therefore, the 3-stage technology in this study is an acceptable solution when it comes to application of coagulation/flocculation and fenton/ozone processes for plating wastewater treatment.

3.4. Removal efficiencies using synthesized wastewater with the Fenton/ozone reaction process

The experiments for testing the treatment process used synthesized wastewater containing Na₂EDTA, $CuSO_4.5H_2O$, $NiSO_4.6H_2O$ and NH_4Cl. The initial water quality parameters of the synthesized wastewater were COD 3440 mg/L, NH_4^+ 150 mg/L, Cu 300 mg/L and Ni 50 mg/L. The best conditions for real plating wastewater treatment are noted in Sections 3.1 and 3.2. These were applied to treat synthesized wastewater and the outcomes are shown in Table 2. Surprisingly, the treatment process's efficiency in removing impurities was much poorer than that of real plating wastewater treatment. This could be explained by the hypothesis that during the electrolysis of the plating procedure the organic-metal complexes of EDTA-Cu and EDTA-Ni, the electrolysis process might weaken the stability of complexes.

3.5. Changes in oxidation – redox potential (ORP) and solution pH during the Fenton/ozone and coagulation/flocculation processes

To optimize and calculate the optimal chemicals in AOPs, the oxidation-reduction potential (ORP) and pH values in the Fenton/ozone solution were determined. The results are shown in Table 3 which depicts that the influent wastewater for ORP and pH values were 435 mV and 3.08, respectively. After the coagulation/flocculation process, the ORP value fell to 273 mV as the process removed a certain amount of oxidants in the solution. Meanwhile the pH value increased to 9.27 due to the pH adjustment to 10 before the coagulation/flocculation process was conducted. This was done to meet the optimal conditions required for the removal of heavy metals and other contaminants. During the Fenton/ozone process, chemicals (Fe^{2+} and H_2O_2) and ozone gas were added contributing to the rise of ORP values (520 mV after Fenton and 516 mV after the ozone process). In the oxidation process, pH was adjusted to the optimal values at around 3 and 6. For the last treatment step, solution pH was adjusted to pH 10 for coagulation and flocculation

Table 3

Changes of ORP values during the Fenton/ozone and coagulation/flocculation processes.

Parameter	Influent wastewater	After Coagulation and flocculation 1	After Fenton process	After ozone	After Coagulation and flocculation 2
ORP	435	273	520	516	−27
pH	3.08	9.27	2.73	5.74	8.88

Table 2

Remaining concentrations of contaminants and removal efficiencies in treating synthesized wastewater.

Treatment process	COD (mg/L)	Removed COD (%)	NH_4^+ (mg/L)	Removed NH_4^+ (%)	Cu (mg/L)	Removed Cu (%)	Ni (mg/L)	Removed Ni (%)
Synthesized wastewater	3440	0	150	0	300	0	50	0
Coagulation and flocculation 1	1800	47.7	135.55	9.6	98.5	67.2	40.34	19.3
Fenton	1120	67.4	97.11	35.3	62.6	79.1	33.63	32.7
Ozone	656	80.9	66.7	55.5	36.4	87.9	32.33	35.3
Coagulation and flocculation 2	452	86.9	61.3	59.1	8.1	97.3	31.5	37

2. Observed consequences of ORP and pH values were -27 mV and 8.88, respectively. These outcomes are suitable with the AOPs and treated wastewater was alkaline and environmentally friendly with reference to the ORP with a negative value.

3.6. Mechanism for degrading EDTA-Ni and EDTA-Cu in plating wastewater by Fenton/ozone

The removal mechanisms of Ni and Cu from plating wastewater are proposed in Fig. 8. According to Huang et al. [4], a glycine pathway was considered the main route for the de-complexation of metal-EDTA. In their study, several intermediates during the process have been proposed such as ethylenediamine, glycine, formamide, acetic acid, oxalic acid, formic acid, CO_2 and H_2O [4]. In present study, the HPLC spectrums have supported the mechanisms. The peaks at retention time(s) (RT) of 2.749 and 3.733 min represent EDTA-Cu and EDTA-Ni. These significantly declined during the treatment process. Especially, the intensity peak at RT 2.749 min reduced significantly in the coagulation/flocculation 1, Fenton, ozone, and coagulation/flocculation 2 (Fig. 9). The increase in peak intensity at RT 3.733 min represents the addition of organic matter to the solution. The results of GC–MS of intermediates in solution after Fenton reaction were shown in Fig. 10 and Appendix. The intermediates in the sample after Fenton reaction were detected such as N-(trimetylsilyl) acetamine at RT 6.099 min, trimethylsilyl chloroacetate at RT 6.544 min, silane (trimethylphenoxy-) at RT 10.532, 12.331 and 13.732 min, propanoic acid at RT 10.960 min, acetic acid at RT 11.518 min, benzoic acid at RT 16.646 min, butanedioic acid at RT 18.504 min, butanoic acid at RT 20.652 min, parabanic acid at RT 21.252 min (Table 4 and Appendix). The intermediates reduced and mostly disappeared after ozone treatment process. This was shown in GC–MS spectrum of after ozone reaction sample was almost same as the bank (spectrum of DI water) (appendix). These results demonstrated that the degradation of EDTA-Cu and EDTA-Ni by Fenton/Ozone generate intermediates. The decomposition of the organic compounds took place continuously and completely finished at the optimal conditions of Fenton/Ozone processes. These results were also agreed with the hypothesis that Fenton is more effective for de-complexation and ozone is more effective for mineralization. Firstly, Fenton reaction is responsible for de-complexing the EDTA-metal complexes and decomposing of more stable organic compounds such as ethylenediamine, glycine, formamide. Subsequently, ozone helps to degrade the remaining and weaker compounds such as N-(trimetylsilyl) acetamine, trimethylsilyl chloroacetate, silane (trimethylphenoxy-), propanoic acid, acetic acid, benzoic acid, butanedioic acid, butanoic acid, parabanic acid. Hence, the integrated combination of Fenton and Ozone methods have achieved the advantage of complementarity.

4. Conclusion and recommendations

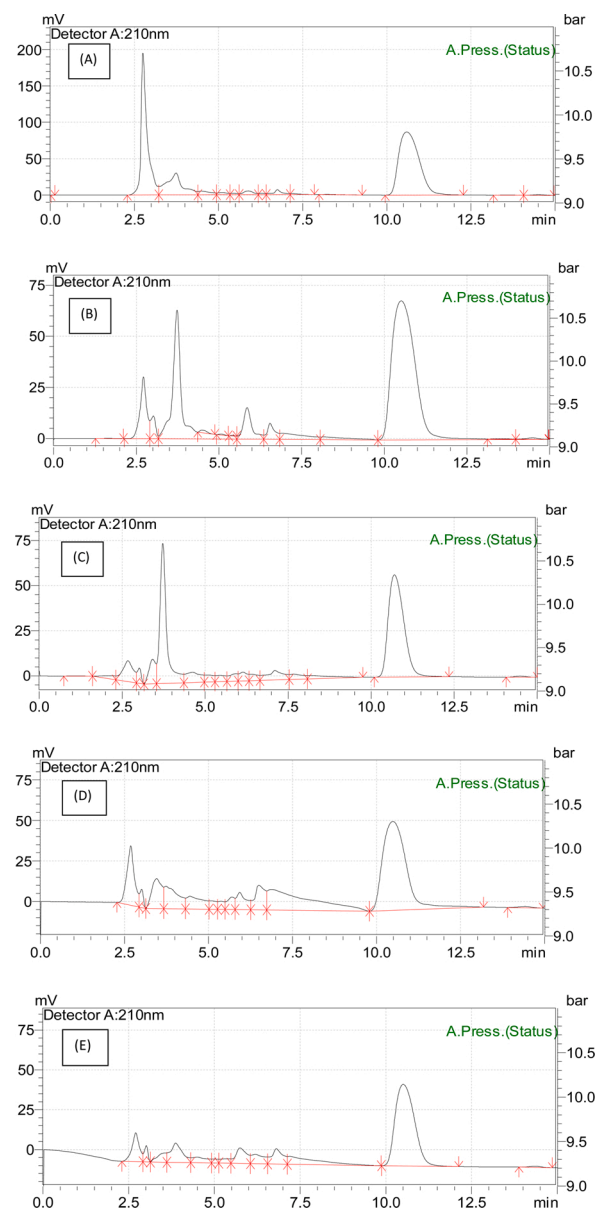In this study, the combined Fenton/Ozone-based oxidation and

Fig. 9. HPLC chromatograms of initial and treated wastewater at various stages: (A) initial wastewater; (B) after coagulation/flocculation 1; (C) after Fenton reaction; (D) after ozone reaction; (E) after coagulation/flocculation 2.
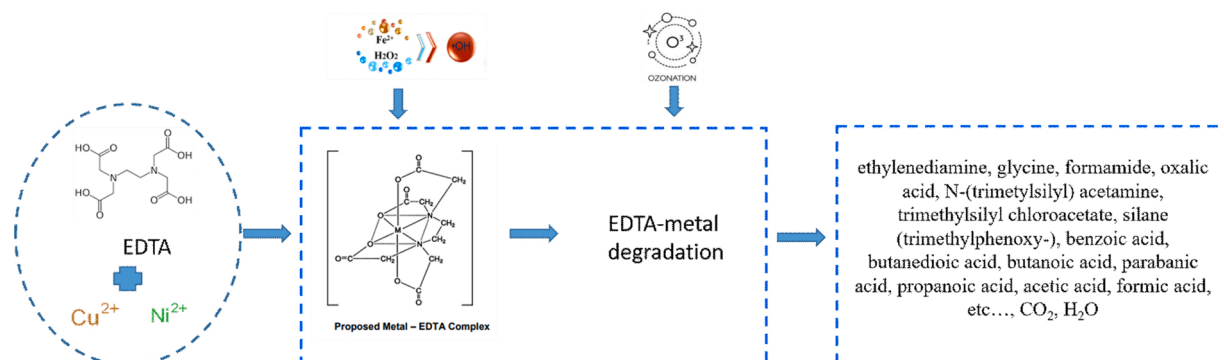

Fig. 8. Proposed mechanism for removing EDTA-Cu, EDTA-Ni by the Fenton/ozone oxidation process.
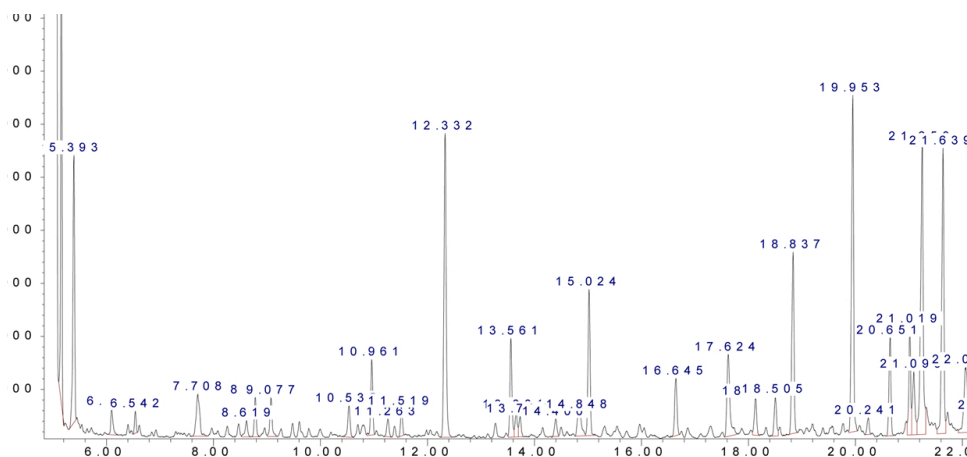
Fig. 10. GC–MS chromatograms of wastewater after Fenton reaction.

Table 4
Main intermediates of degradation process of EDTA-Cu and EDTA-Ni after Fenton reaction.

No.	Retention time (RT) (min)	Name	% Area
1	6.099	N-(trimetylsilyl) acetamine	0.39
2	6.544	trimethylsilyl chloroacetate	0.23
3	10.532, 12.331 and 13.732	silane (trimethylphenoxy-)	0.49; 4.43; 0.3
4	10.960	propanoic acid	0.97
5	11.518	acetic acid	0.34
6	16.646	benzoic acid	0.85
7	18.504	butanedioic acid	0.59
8	20.652	butanoic acid	1.29
9	21.252	parabanic acid	4.81

coagulation process could effectively remove metals-EDTA plating wastewater. The optimal 3-stage reaction conditions for treating the real plating wastewater was applicable. Optimal conditions for plating wastewater treatment were found: (1) coagulation and sedimentation: adjusted to pH 10, 1200 mg Fe and 2.4 mL PAA; rapid sedimentation; (2) Fenton + ozone: 1200 mg Fe +20 mL H_2O_2, stirring for 10 min, ozone aeration/ozonation in 20 min, adjusted pH level 6–8; continuous ozone aeration/ozonation in 25 min; and (3) coagulation and sedimentation: pH 10, 3.2 mL PAA, rapid sedimentation. This technique is highly efficient for the removal of metals in real plating wastewater rather than in the synthesized experiments. These AOPs could treat complex metals in wastewater with different characteristics and concentrations of heavy metals in the treated effluent met the Vietnam national technical regulations for discharge. Mechanisms of the degradation of EDTA-metal complexes were proposed. The intermediates of decomposition process of the chelates were detected by GC–MS and they mostly disappeared in the after ozone reaction. For further studies, it is crucial to analyze the elemental and mineral composition of precipitates employing treatment processes, such as XRD and XRF. Characterizing the sludge generated from traditional technology and sludge generated in this treatment procedure will help assess the quantity of recoverable metals, methods of metal recovery, and usage of sludge.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgements

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jwpe.2020.101836.

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