Application of Ferrate(VI) on the Decomplexation of Cu(II)-EDTA

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Abstract

In this study, Fe(VI) was employed as a multi-functional agent to treat the simulated industrial wastewater contaminated with Cu(II)-EDTA through oxidation of EDTA, decomplexation of Cu(II)-EDTA and subsequent removal of free copper through precipitation. The decomplexation of 10^{-4} M Cu(II)-EDTA species was performed as a function of pH at excess concentration of Fe(VI). It was noted that the acidic conditions favor the decomplexation of Cu(II)-EDTA as the decomplxation was almost 100% up to pH 6.5, while it was only 35% at pH 9.9. The enhanced degradation of Cu(II)-EDTA with decreasing the pH could be explained by the different speciation of Fe(VI). $HFeO_4^-$ and H_2FeO_4, which are relatively more reactive than the unprotonated species FeO_4^{2-}, are predominant species below neutral pH. It was noted that the decomplexation reaction is extremely fast and within 5 to10 min of contact, 100% of Cu(II)-EDTA was decomplexed at pH 4.0. However, at higher pH (i.e., pH 10.0) the decomplexation process was relatively slow and it was observed that even after 180 min of contact, maximum *ca* 37% of Cu(II)-EDTA was decomplexed. In order to discuss the kinetics of the decomplexation of Cu(II)-EDTA, the data was slightly fitted better for the second order rate reaction than the first order rate reaction in the excess of Fe(VI) concentration. On the other hand, the removal efficiency of free Cu(II) ions was also obtained at pH 4.0 and 10.0. It was probably removed through adsorption/coagulation with the reduced iron i.e., Fe(III). The removal of total Cu(II) was rapid at pH 4.0 whereas, it was slow at pH 10.0. Although the decomplexation was 100% at lower pH, the removal of free Cu(II) was relatively slow. This result may be explicable due to the reason that at lower pH values the adsorption/coagulation capacity of Fe(III) is greatly retarded. On the other hand, at higher pH values the decomplexation of Cu(II)-EDTA was partial, hence, slower Cu(II) removal was occurred.

Keywords: Fe(VI), Cu(II)-EDTA, Decomplexation, Kinetics, Oxidation

1. Introduction

The multifunctional nature of ferrate(VI) (i.e., potential oxidant, coagulant, disinfectant along with the non-toxic by products) has received an increased attention for the treatment of waste/effluent waters in recent past. Because of its non-toxic nature, the ferrate(VI) is to be termed as a 'GreenChemical'.[1-4] The commonly used chemical oxidants showed their limitations, e.g., in chlorination and ozonation processes, the trihalomethanes and bromate are to be occurred as harmful disinfectant/disinfection by-products (DBPs).[5,6] Moreover, it requires additional coagulant/adsorbent dose to remove the non-degradable impurities e.g., metallic species etc. On the other hand, the application of ferrate(VI) possess relatively higher oxidizing/disinfection capacity and the reduced Fe(VI) into Fe(III) is one of potential coagulant/adsorbent, can serve to remove the non-degradable impurities, and the entire treatment process is to be free from any DBPs. Hence, it may be a potential alternative for such waste/effluent water treatments.

Ethylenediamine tetraacetic acid (EDTA) is widely used for various industries viz., metal plating, nuclear, pharmaceutical, food, photography, pulp/paper processing, and textiles because of its strong complexing nature with metal ions.[7] The EDTA complexed metallic species are found to be soluble over the entire pH region and showed enhanced mobility of these metallic species in solution, hence, the treatment of such metal-EDTA containing wastes is one of the important research endeavors.[8]

Decomplexation of metal-EDTA being the prerequisite in the treatment of metal-EDTA containing wastes as well as control of heavy metal, several techniques have been applied.[9-15] Literature survey reveals that the biodegradation of EDTA was carried out and the liberation of free metal ions showed lower mobility under neutral conditions.[9] Ferric chloride was used to

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remove the copper and zinc in the municipal waste water in which these metal ions are complexed with EDTA.[10] The process was demonstrated that copper and zinc were adsorbed on ferric hydroxide, however, the waste contained the soluble Fe-EDTA⁻ species. TiO$_2$-mediated photocatalytic treatment was reported to deal with wastes containing EDTA complexed metal ions.[11-14] Similarly, few reports and our own work dealt with the adsorption of metal-EDTA species onto the surface of TiO$_2$ solid.[7,16] Non-dispersive solvent extraction process was also reported for the removal of EDTA complexed copper from aqueous solutions.[15] These reported methods seem either expensive or inadequate for the complete treatment of wastes contaminated with metal complexed EDTA.

Hence, in a quest for efficient and more environment-friendly treatment technologies, Fe(VI) has much attention as a multi-functional agent in the treatment of metal complexed organics. We already have explored the possibilities of Fe(VI) in the environmental remediation processes particularly the treatment of cyanide and metal complexed cyanide wastes and was found to be efficient for such treatments.[17,18] A few reports also enabled the treatment of Zn-cyanide complex.[19] Therefore, in this study, Fe(VI) was employed as a multi-functional agent to treat the simulated industrial wastewater contaminated with Cu(II)-EDTA through oxidation of EDTA, decomplexation of Cu(II)-EDTA and subsequent removal of free copper through adsorption/coagulation. The goal of this study is in the investigation for the decomplexation of Cu(II)-EDTA and simultaneous removal of free Cu(II) from aqueous solutions using the ferrate(VI).

2. Materials and Methods

2.1. Reagents and Materials

CuSO$_4$·5H$_2$O: GR grade was obtained from Duksan Pure Chem. Co. Ltd., Korea and ethylene diaminetetraacetic acid disodium salt (Na$_2$EDTA) was obtained from Showa Chem. Co. Ltd., Japan. The water (15 MΩ cm) used for sample preparations was purified using a Milli Q-Plus Instrument (Millipore SA 67120, Molshiem, France). The stock solutions (1.0 mmol/L) of copper and EDTA were prepared in this water. The stock solutions were further diluted as and when required. All other chemicals used were AR/GR grade unless otherwise mentioned.

2.2. Preparation of Potassium Ferrate

Potassium ferrate was prepared by adopting the method[20] with some modifications as described elsewhere.[18] The purity of the dried potassium ferrate(VI) was checked by preparing an aqueous solution at pH 9.2 (phosphate buffer) and recording the absorbance at 510 nm using a UV-Visible spectrophotometer (OPTIZEN 2120UV, Macasys Co. Ltd., Korea) with the standard molar absorbance 1150 M^{-1} cm^{-1} at 510 nm at pH 9.2 which showed that the purity of the Fe(VI) was in excess of 98%.[4]

2.3. Experimental Methods

The decomplexation of Cu(II)-EDTA was carried out at different pHs (pH 4 and 10), mixing 0.10 mmol/L Cu(II)-EDTA with 2.4 mmol/L ferrate for 60 min. The ionic strength in the solution was fixed as 0.01 M with NaNO$_3$. The initial pH of the solution was adjusted using 0.01 M HNO$_3$ or 0.01 M NaOH. The solution pH was maintained within ±0.1 of the desired value using the 0.01 M NaOH or 0.01 M HNO$_3$ during the reaction period. Aliquots of the solution were periodically removed from reactors and rapidly filtered through 0.45 µm membrane filters. Then the samples were kept in the refrigerator before the analysis.

2.4. Analytical Methods

The 1.0×10^{-4} mol/L of Cu(II)-EDTA solution was taken in a beaker and the pH was adjusted to a specified value by adding the drops of conc. HNO$_3$/NaOH solutions. Then, a known amount of Fe(VI) was introduced under the stirring condition, and the change in concentration of Cu(II)-EDTA was checked with the help of ion chromatograph (Metrhom Modular IC System) which was calibrated previously with the known concentrations of Cu(II)-EDTA at the same pH. The results were obtained as a function of time and at different pH. Similarly, the change in total copper concentration was checked after filtration of Fe(VI) treated samples using 0.45 µm syringe filter and was analyzed by the AAS (Varian A-300). The pH measurement was done using Orion pH meter unit 720A, USA.

3. Results and Discussion

3.1. Effect of pH on Cu(II)-EDTA Decomplexation

The decomplexation of Cu(II)-EDTA was carried out at different pH keeping the Cu(II)-EDTA concentration 0.10 mmol/L as constant and the ferrate dose 2.4 mmol/L. The sample solutions were stirred for 60 min and then analyzed for the Cu(II)-EDTA using ion chromatograph and the results obtained were shown graphically in Fig. 1. It is to be noted that the acidic condition favors the decomplexation of Cu(II)-EDTA; while the decomplxation maintained almost 100% up to pH 6.5, it was only ca 35% at pH 9.9. This suggests that the decomlexation process is highly acid catalyzed. Moreover, it was also reported and observed that the protonated species of ferrate(VI) i.e., HFeO$_4$⁻ and H$_2$FeO$_4$ are comparatively more reactive than the deprotonated species FeO$_4$$^{2-}$.[19,21] Yang and Davis also reported favorable decomplexation of Cu(II)-EDTA at lower pH from photocatalytic oxidation (PCO) with illuminated TiO$_2$.[13] As EDTA had two types of ligand such as amine and carboxyl groups, they reported that PCO reactions are initiated at either a carboxyl or amine group, depending on pH. At lower pH, the PCO reaction proceeded favorably via radical formation at a carboxyl group complexed to the TiO$_2$ surface.[14] Lockhart and Blakeley reported the formation of ED3A (ethylenediaminetriacetic acid) during aerobic photodegradation of Fe(III)-EDTA.[22]

Various protonated and deprotonated species of ferrate(VI) are present in solution and these species are prevalent at differ-
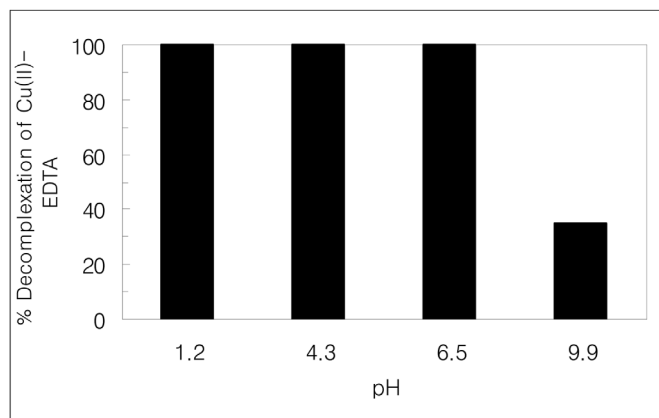
Fig. 1. Decomplexation of Cu(II)-EDTA at various pH values [Initial Cu(II)-EDTA concentration: 0.10 mmol/L; Fe(VI) dose: 2.4 mmol/L].
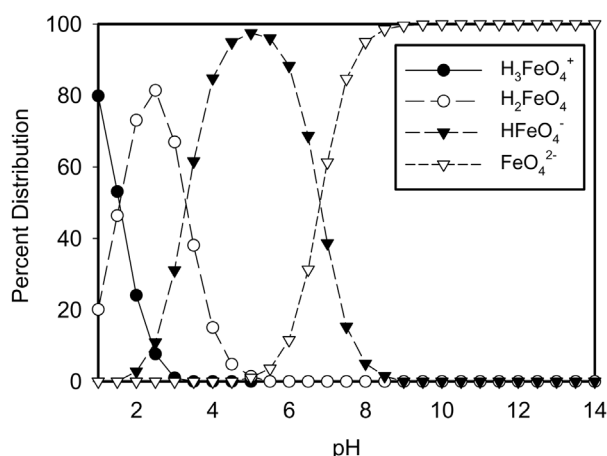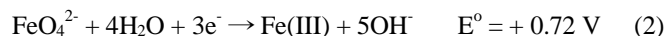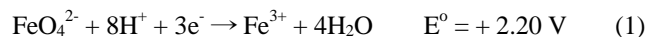

Fig. 2. Speciation of ferrate(VI) species in aqueous solutions [Concentration of Fe(VI): 2.4 mmol/L].

ent solution pH. Fig. 2 depicts the percentage speciation of these species with variation of solution pH. The speciation was calculated using MINEQL software using known pK_a's values (i.e., $pK_{a1} = 1.6$, $pK_{a2} = 3.5$ and $pK_{a3} = 7.3$) at the constant Fe(VI) concentration of 2.4 mmol/L.[2,23] This figure clearly indicates that $HFeO_4^-$ and FeO_4^{2-} are predominant in neutral and alkaline pH, in which Fe(VI) was known to be relatively stable towards its spontaneous decomposition to ferric ion (Fe(III)), as also observed in our studies as well.[24] The figure also indicate that at pH~10 the only species i.e., FeO_4^{2-} exists in aqueous solutions. As Cu(II)-EDTA is a strong chelating complex, most species of Cu(II) complexed with EDTA in the pH ranges study presented as Cu(II)-EDTA. Otherwise, two forms of Fe(VI), namely, $HFeO_4^-$ (85%) and H_2FeO_4 (15%), as shown in Fig. 2, can react with Cu(II)-EDTA at pH 4. However, at pH 10, as most ferrate is present as $HFeO_4^{2-}$, a single species of Fe(VI) can react with Cu(II)-EDTA. The rapid decomplexation of Cu(II)-EDTA at pH 4 compared to pH 10 is probably resulted from different speciation of Fe(VI). $HFeO_4^-$ and H_2FeO_4, which are regarded as relatively more reactive species than the unprotonated species FeO_4^{2-}, are predominant species below neutral pH. Also the redox potential of ferrate(VI) is comparatively very high in acidic medium as compared to the alkaline medium which can be seen

from the reduction potentials of reactions (1) and (2) in acidic and alkaline solutions.[4] Therefore a powerful oxidizing condition is provided at the elevated concentration of the Fe(VI) species such as $H_3FeO_4^+$ and H_2FeO_4.

$$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O \qquad E^o = + 2.20\ V \qquad (1)$$

$$FeO_4^{2-} + 4H_2O + 3e^- \rightarrow Fe(III) + 5OH^- \qquad E^o = + 0.72\ V \qquad (2)$$

3.2. Kinetics of Cu(II)-EDTA

Kinetics of the decomplexation of Cu(II)-EDTA was observed as a function of time and at two different pH (i.e., 4.0 and 10.0). The initial Cu(II)-EDTA concentration was kept constant at 0.10 mmol/L, and the ferrate(VI) dose was at 2.40 mmol/L. Results obtained were shown in Fig. 3. It was noted that at lower pH (i.e., pH 4.0) the decomplexation reaction is extremely fast, and 100% of Cu(II)-EDTA was decomplexed within 5 to 10 min of contact. However, at higher pH (i.e., pH 10.0) the decomplexation process was relatively slow and it was observed that even after 180 min of contact, maximum ca 37% of Cu(II)- EDTA was decomplexed. Since, the decomplexation of Cu(II)- EDTA was seemingly very fast at lower pH hence, the data obtained at higher pH was used to discuss the kinetics of the decomplexation. As TiO_2-mediated photocatalytic treatment has been widely used to deal with wastes containing EDTA complexed metals ions, the percentage disappearance of Cu(II)-EDTA by ferrate (VI) was compared with that by TiO_2-mediated photocatalysis.[13] Yang and Davis reported that the aqueous initial decomplexation rate (r_{aq}) of Cu(II)-EDTA at pH 4, developed from the linear portion of all aqueous Cu(II)-EDTA concentrations with respect to time from 0 to 10 min, was 3.0×10^{-6} mol/ L/min.[13] However, the aqueous initial decomplexation rate (r_{aq}) of Cu(II)-EDTA by ferrate(VI) at pH 4 was 7.5×10^{-6} mol/L/min, suggesting ferrate(VI) is more efficient oxidant than TiO_2-mediated photocatalytic reaction in the decomplexation of Cu(II)-EDTA at acidic condition.

Moreover, the simultaneous Cu(II) removal was also observed at these two pH values. It was assumed that with the reduction
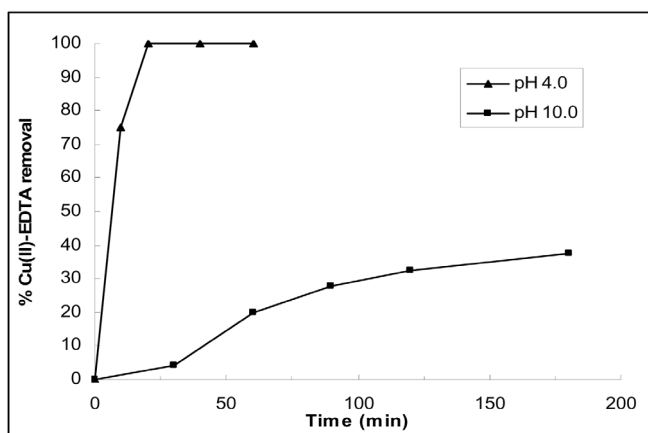

Fig. 3. Kinetics of the decomplexation of Cu(II)-EDTA as a function of time at different pH values [Initial Cu(II)-EDTA concentration: 0.10 mmol/L; Fe(VI) dose: 2.4 mmol/L].
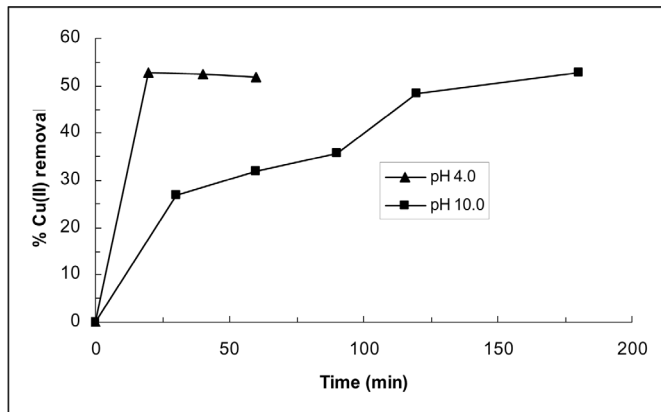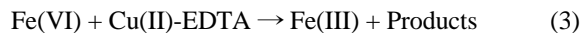
Fig. 4. Simultaneous removal of Cu(II) from the aqueous solutions after the ferrate(VI) treatment to Cu(II)-EDTA at different pH values [Initial Cu(II)-EDTA concentration: 0.10 mmol/L; Fe(VI) dose: 2.4 mmol/L].

of Fe(VI) into Fe(III), it may help to adsorb/coagulate the free Cu(II) ions in solution. The solution was filtered with 0.45 µm syringe filter, and the Cu(II) content was analyzed using AAS. The results obtained are shown in Fig. 4. Again, the removal of free Cu(II) ions was rapid at lower pH (i.e., pH 4.0) whereas, it was slow at higher pH (i.e., 10.0). Moreover, maximum *ca* 52% of Cu(II) was removed from the solution at either of the pH i.e., pH 4.0 or 10.0. Decomplexation of 100% at lower pH, but slow removal of free Cu(II) may be explicable due to the reason that at lower pH values the adsorption/coagulation capacity of Fe(III) is greatly retarded.[25] On the other hand, at higher pH values the decomplexation of Cu(II)-EDTA was partial, hence, lower Cu(II) removal was occurred.

Further, in order to obtain a quantitative information for the decomplexation of Cu(II)-EDTA in aqueous phase, the following simple irreversible reaction, expressed as equations (3) and (4) below, was assumed to occur.

$$Fe(VI) + Cu(II)\text{-}EDTA \rightarrow Fe(III) + Products \qquad (3)$$

$$-\frac{d[Cu(II)-EDTA]}{dt} = k\,[Fe(VI)]^m\,[Cu(II)-EDTA]^n \qquad (4)$$

Where k represents the overall rate constant of the reaction (3) and the [Fe(VI)] and [Cu(II)-EDTA] are the molar concentrations of Fe(VI) and Cu(II)-EDTA, respectively, m and n are the orders of the reaction with respect to the reactant. Since, the concentration of Fe(VI) was 24 times higher than that of Cu(II)-EDTA, under pseudo-first-order condition, we may write the equation 4 as:

$$-\frac{d[Cu(II)-EDTA]}{dt} = k_1[Cu(II)-EDTA]^n \qquad (5)$$

where $k_1 = k\,[Fe(VI)]^m$

The change in concentration of Cu(II)-EDTA was analyzed as a function of time and tried to simulate the data for first and second order reaction equations (Figs 5 and 6), but observed
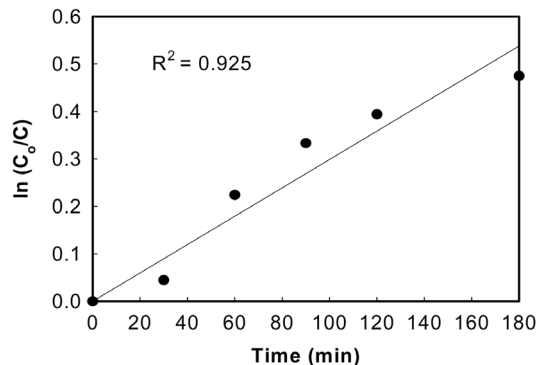

Fig. 5. First order rate kinetics (i.e., ln (C$_o$/C) *vs* time (min)).
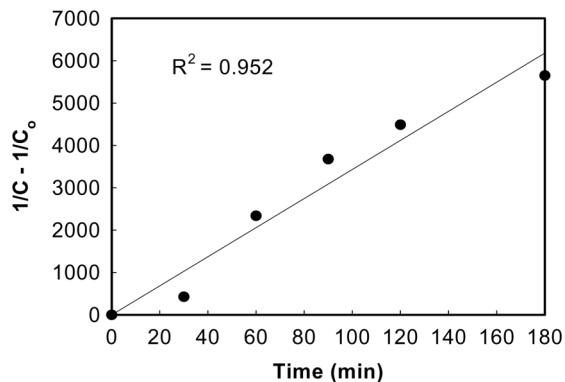

Fig. 6. Second order rate kinetics (i.e., (1/C - 1/C$_o$) *vs* time (min))

values were slightly fitted well with the second order rate equation (correlation coefficient: 0.952) than the first order rate equation (correlation coefficient: 0.925). Hence, it may be concluded that under the condition stated, further detailed researches are needed to elucidate the rate of decomplexation of Cu(II)-EDTA.

4. Conclusions

Ferrate(VI) was attempted to degrade the Cu(II)-EDTA complex at various pH values (i.e., acidic to alkaline regions) and it was found that decomplexation of Cu(II)-EDTA with ferrate(VI) was highly acid catalyzed and almost 100% decomplexation took place in the acidic conditions. However, at higher pH it was retarded significantly. Moreover, the kinetics of degradation was discussed at higher pH 10 and it was observed that under the condition of very high Fe(VI) concentration, the decomplexation reaction generally well described by second order rate law. The simultaneous Cu(II) removal by adsorption/coagulation with Fe(III) was also estimated.

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