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*Short Communication*

# Optimization for the Degradation of Isonicotinohydrazide by Electrochemical Oxidation

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In this study, a novel typical transition elements co-doped lead dioxide electrode was prepared by the thermal decomposition and electro-deposition technique for the treatment of pharmaceutical wastewater. Isonicotinohydrazide was selected as the model pollutant for it is the first-line medication in prevention and treatment of tuberculosis and the effects of operational factors were investigated. The optimized operational factors were achieved by investigating on the effects of different parameters, such as doped transition elements ratios, electrolyte concentration, current density and isonicotinohydrazide initial concentration. The isonicotinohydrazide could be almost completely removed and satisfied mineralization was achieved on the optimized conditions of current density 30 $mA/cm^2$, 0.1 mol/L $Na_2SO_4$ and 100 mg/L isonicotinohydrazide initial concentration. This paper can provide basic data and technique reference for the pharmaceutical wastewater pollution control.

**Keywords:** electrochemical oxidation; pharmaceutical wastewater; isonicotinohydrazide

## 1. INTRODUCTION

Huge number of pharmaceutical wastewater is produced in China every year, this kind of wastewater containing different toxic organic compounds, which would lead to severe environmental problems without suitable treatment. Due to the toxic of the pharmaceutical wastewater, traditional treatment methods, such as biological treatment and coagulation, could not reach satisfied results. Take isonicotinohydrazide for example, this kind of highly concentrated wastewater treatment is still mainly used biological system at present, but the results can not reach the increasingly stringent discharge standard [1-2]. Therefore, it is urgent to seek sound way for this kind of wastewater treatment [3-6].

Advanced Oxidation Processes (AOPs) can receive good results for pharmaceutical wastewater with the formation of hydroxyl radical, which can react with kinds of organics. As a typical AOP,

electrochemical oxidation technology has been applied in wastewater pollution control due to good treatment effects at relatively mild reaction conditions [7-10]. The $PbO_2$ electrode has showed satisfied stability and high catalytic activity in organic wastewater treatment [11-12]. In recent year, the transition element has showed the advantages in the enhancement of high catalytic efficiency [13-14], thus relatively highly catalytic efficiency can reach with the transition element doped $PbO_2$ electrode.

In this paper, Al and Zn were selected as typical transition elements, which were used to enhance the catalytic activity of the $PbO_2$ electrode and the novel Al/Zn doped $PbO_2$ electrodes were prepared. The effects of different operational factors in electrochemical oxidation were optimized and relative good results achieved, which showed that electrochemical oxidation can be used for pharmaceutical wastewater pollution control.

## 2. MATERIALS AND METHODS

### *2.1. Materials*

The $PbO_2$ film of electrodes was prepared by the electro-deposition technique. Metal element (Al and Zn) was added into the solution for the electrodeposition of the Al/Zn doped $PbO_2$ electrode, and the amounts were based on the mole ratio with Pb element.

Isonicotinohydrazide (CAS number 54-85-3) was selected as the typical pharmaceutical pollutant because it is the first-line medication in prevention and treatment of tuberculosis, which is also widely existed in pharmaceutical wastewater.

### *2.2. Methods*

The electrochemical oxidation system was mainly composed by two working electrodes with the active area of $70\times20$ $mm^2$, and the electrolysis cell working volume was 250 mL.

The concentration of isonicotinohydrazide was measured by high performance liquid chromatography (1200, Agilent Technologies, USA) with the detection wavelength at 263 nm. A mixture of ultra water containing 0.02 mol/L concentrated disodium hydrogen phosphate and methanol with the ratio of 96:4 (v/v) was used as the mobile liquid phase at a flow rate of 1.0 mL/min. The chemical oxygen demand (COD) was measured by the dichromate method (DRB200, Hach, USA).

## 3. RESULTS & DISCUSSION

### *3.1 Effect of different doped amount of Al and Zn*

Three Al and Zn co-doped electrodes were prepared, including Al:Zn=1:3 (Pb:Al=100 mol:0.5 mol, Pb:Zn=100 mol:1.5 mol), Al:Zn=2:2 (Pb:Al=100 mol:1.0 mol, Pb:Zn=100 mol:1.0 mol) and Al:Zn=3:1 (Pb:Al=100 mol:1.5 mol, Pb:Zn=100 mol:0.5 mol). The effects of three different Al and Zn

co-doped electrodes were explored. As were shown in Figure 1, the effects of three different Al and Zn co-doped $PbO_2$ were studied on the degradation of 100 mg/L isonicotinohydrazide on condition of 0.1 mol/L $Na_2SO_4$ and 30mA/cm$^2$ current density.

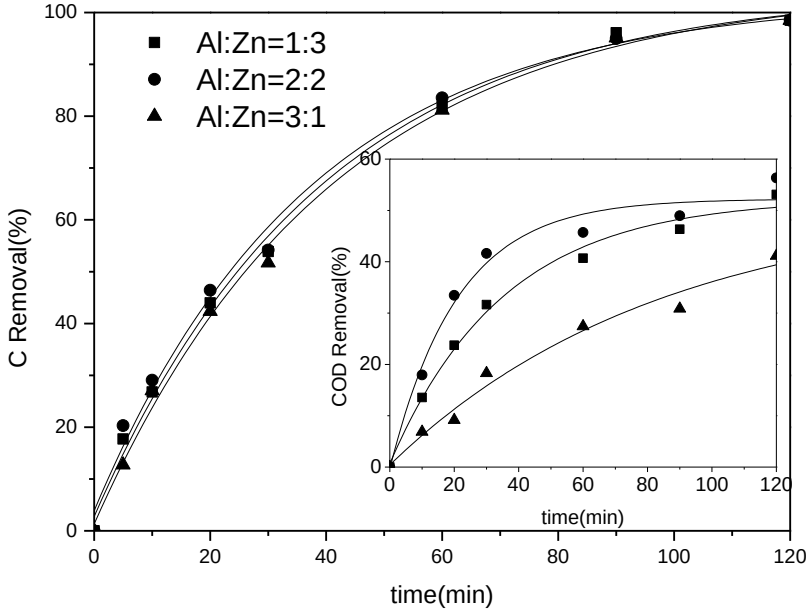


**Figure 1.** The effects of different electrodes on degradation of isonicotinohydrazide

As were shown in Figure 1, after 120 min treatment, the isonicotinohydrazide could be removed all above 98%, which showed that the structure of the pollutant could be destroyed after 2 h treatment. As for COD removal, after 120 min reaction, the effect of Al:Zn=2:2 could reach 56.33%, while those of Al:Zn=1:3 and Al:Zn=3:1 were 53.11% and 41.15%, respectively. The results also showed that the with Al:Zn=2:2 electrode, relative good results could be achieved for the mineralization of the organics.

*3.2 Effect of current density*

The effect of different current density (15, 30, 50 and 70 mA/cm$^2$) on the degradation of 200 mg/L isonicotinohydrazide was investigated at 0.1 mol/L $Na_2SO_4$ and Al-Zn co-doped electrode (Al:Zn=2:2). The results were shown in Figure 2.

Figure 2 showed the degradation of isonicotinohydrazide on concentration and COD removal on different current density on condition of 100 mg/L isonicotinohydrazide, 0.1 mol/L $Na_2SO_4$ and pH=7. At the current density of 15 mA/cm$^2$, 30 mA/cm$^2$, 50 mA/cm$^2$ and 70 mA/cm$^2$, the isonicotinohydrazide could almost be total degraded after 120 min treatment, while the COD removals were 30.88%, 43.04%, 52.71% and 73.66%, respectively. These results also showed that the COD removal rates increased obviously with the increase of current density from 15 mA/cm$^2$ to 70 mA/cm$^2$. The intermediates were detected during the electrochemical oxidation and the products mainly include benzodiazepines and kinds of organic acids. Compared the results of concentration with COD removal

data, the conclusion could be got that high current density could significantly promote the isonicotinohydrazide degradation [15-16].

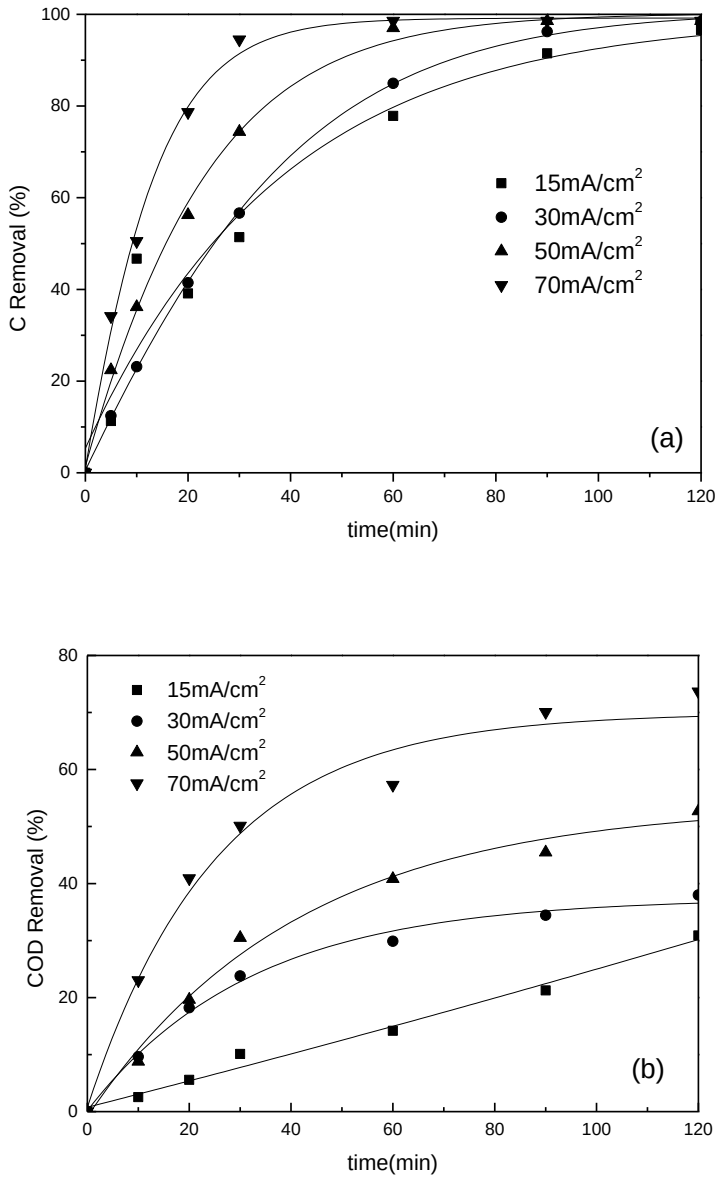


**Figure 2.** The effects of current density on degradation of isonicotinohydrazide: (a) Concentration, (b) COD

However, there existed the byproduct reaction of oxygen evolution, and with the increase of current density, the oxygen evolution reaction would enhance, which would significant increase the energy consumption. Therefore, combined these factors, 30 mA/cm$^2$ was selected as the optimized current density in our studies.

*3.3 Effect of electrolyte concentration*

Electrolyte concentration is an important factor in electrochemical oxidation system [17-18]. The $Na_2SO_4$ was selected as supporting electrolyte to increase the solution conductivity. Therefore, the

effects of $Na_2SO_4$ concentration of 0.05 mol/L, 0.1 mol/L, 0.2 mol/L and 0.5 mol/L were studied on condition of 100 mg/L isonicotinohydrazide, pH=7 and 30 mA/cm$^2$ current density. The results were shown in Figure 3.

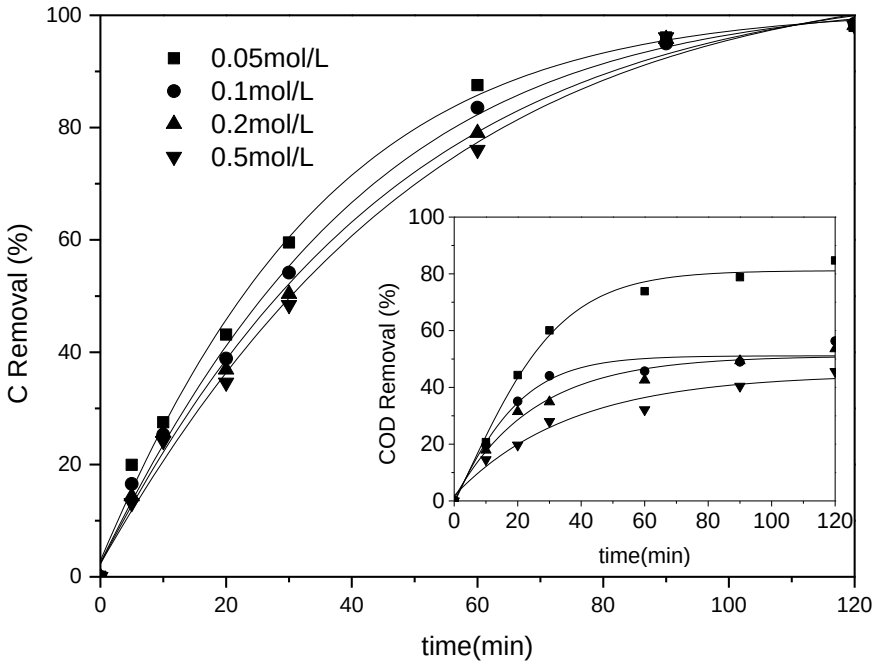


**Figure 3.** The effects of $Na_2SO_4$ concentration on degradation of isonicotinohydrazide

Figure 3 showed the degradation of isonicotinohydrazide with different electrolyte concentration. After 120 min treatment, on condition of electrolyte concentration of 0.05, 0.1, 0.2 and 0.5 mol/L, the isonicotinohydrazide was almost total removed, while the COD removal was 84.73%, 56.33%, 53.62% and 45.60%, respectively. The results showed that an increase in electrolyte concentration could lead to decrease of the mineralization of the pollutants. When at high concentration of $Na_2SO_4$, there must added more electrolyte, which would results in high cost. While at low concentration of electrolyte, there would lead to high electric voltage between the anode and the cathode at the current density, which would also lead to high energy cost. Therefore, 0.1 mol/L $Na_2SO_4$ was an optimized result for electrolyte concentration.

### *3.4 Effect of isonicotinohydrazide initial concentration*

The effects of initial isonicotinohydrazide concentration of 50 mg/L,100 mg/L, 200 mg/L, 500 mg/L, 800 mg/L and 1000 mg/L were investigated on the conditions of 30 mA/cm$^2$, pH=7 and 0.1 mol/L $Na_2SO_4$.

As were shown in Figure 4, isonicotinohydrazide of different concentration was almost total removed after 120 min treatment. As for COD removal, the effect of 50 mg/L, 100 mg/L, 200 mg/L, 500 mg/L, 800 mg/L and 1000 mg/L were 73.37%, 56.33%, 43.04%, 34.02%, 33.77% and 32.88%,

respectively. The results showed that the effect of 50 mg/L was the most obvious, the next was 100 mg/L. Considering the discharged pharmaceutical wastewater in pharmaceutical enterprise, 100 mg/L isonicotinohydrazide initial concentration was the suitable one.

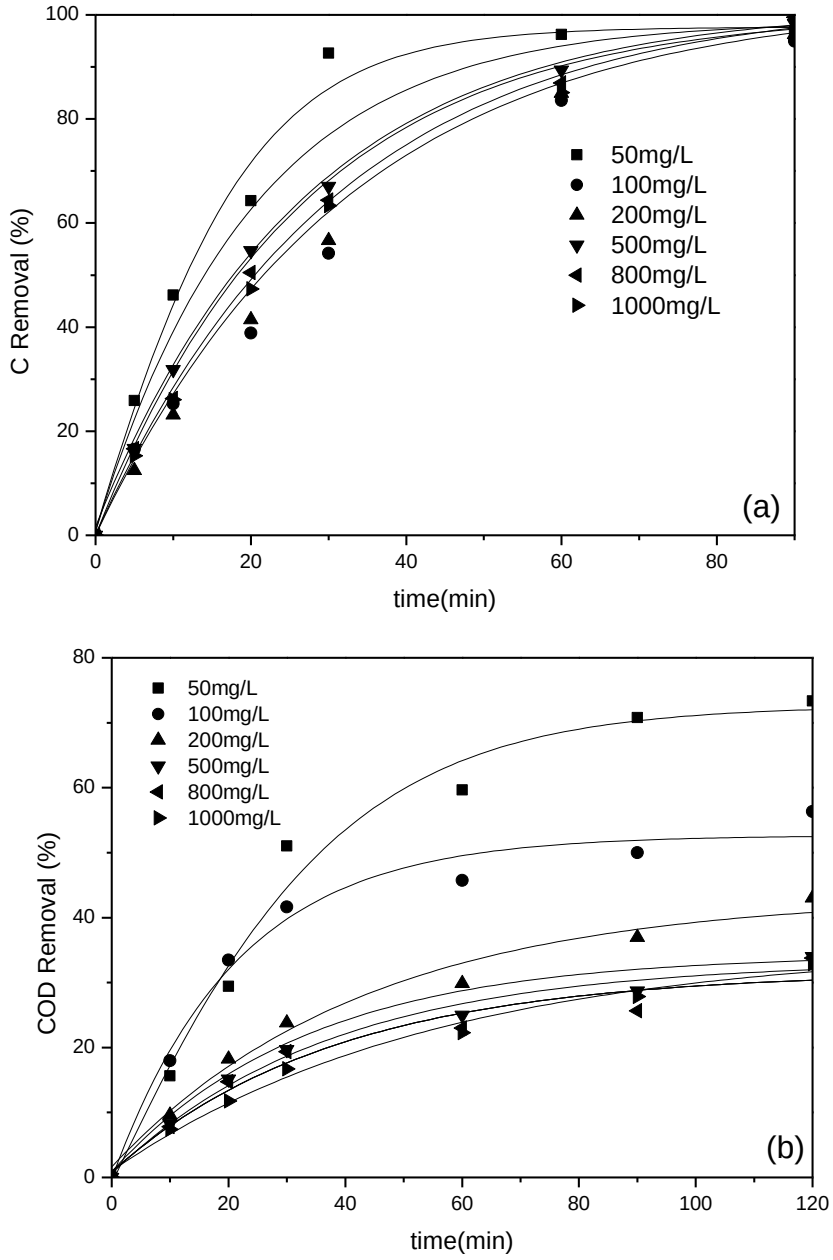


**Figure 4.** The effects of isonicotinohydrazide initial concentration: (a) Concentration, (b) COD

## 4. CONCLUSION

Three Al and Zn co-doped electrodes were prepared, including Al:Zn=1:3 (Pb:Al=100 mol:0.5 mol, Pb:Zn=100 mol:1.5 mol), Al:Zn=2:2 (Pb:Al=100 mol:1.0 mol, Pb:Zn=100 mol:1.0 mol) and Al:Zn=3:1 (Pb:Al=100 mol:1.5 mol, Pb:Zn=100 mol:0.5 mol). The degradation of

isonicotinohydrazide was explored and the effects of operational factors were investigated. The results showed that with Al and Zn co-doped electrode, the isonicotinohydrazide could be degraded completely with satisfied mineralization at the optimized operational condition of 100 mg/L isonicotinohydrazide, 0.1 mol/L $Na_2SO_4$ as electrolyte and current density of 30 mA/cm$^2$. The results showed that electrochemical oxidation was an available way for pharmaceutical wastewater pollution control.

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## References

1. T. Handa, S. Singh, I.P. Singh, *J. Pharmaceut. Biomed.*, 89 (2014) 6
2. X. Yang, R.C. Flowers, H.S. Weinberg, P.C. Singer, *Water Res.* 45 (2011) 5218
3. J. Choi, H. Lee, Y. Choi, S. Kim, S. Lee, S. Lee, W. Choi, J. Lee, *Appl. Catal. B-Environ.*, 147 (2014) 8
4. S. Sathyamoorthy, C.A. Ramsburg, *Chemosphere*, 92 (2013) 639
5. P.J. Phillips, S.G. Smith, D.W. Kolpin, S.D. Zaugg, H.T. Buxton, E.T. Furlong, K. Esposito, B. Stinson, *Environ. Sci. & Technol.*, 44 (2010) 4910
6. S. Farhadi, B. Aminzadeh, A. Torabian, V. Khatibikamal, M.A. Fard, *J. Hazard. Mater.*, 219 (2012) 35
7. C. Comninellis, *Electrochim. Acta*, 39 (1994) 1857
8. J.L. Cao, H.Y. Zhao, F.H. Cao, J.Q. Zhang, *Electrochim. Acta*, 52 (2007) 7870
9. Y.H. Cui, Y.J. Feng, X.Y. Li, *Chem. Eng. Technol.*, 34 (2011) 265
10. Z.H. Liao, F. James, *J. Appl. Electrochem.*, 39 (2009) 1993
11. S.P. Tong, C.A. Ma, H. Feng, *Electrochim. Acta*, 53 (2008) 3002
12. S. Song, J.Q. Fan, Z.Q. He, L.Y. Zhan, Z.W. Liu, J.M. Chen, X.H. Xu, *Electrochim. Acta* 55 (2010) 3606
13. S. Kim, J.K. Noh, S. Yu, W. Chang, K.Y. Chung, B.W. Cho, *J. Electrochem.*, 30 (2013) 159
14. A.P. Jin, W. Chen, Q.Y. Zhu, Z.L. Jian, *Electrochim. Acta*, 55 (2010) 6408
15. J.L. Cao, H.Y. Zhao, F.H. Cao, J.Q. Zhang, C.N. Cao, *Electrochim. Acta*, 54 (2009) 2595.
16. M. Kobya, M. Demirbas, M. Bayramoglu, *Chemosphere*, 132 (2006) 183
17. S. Abaci, K. Pekmez, A. Yildiz, *Electrochem. Commun.*, 7 (2005) 328
18. C.T.J. Low, D. Pletcher, F.C. Walsh, *Electrochem. Commun.*, 11 (2009) 1301