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Research on a new electrochemical method combined with chemical coagulation in removal of lead, zinc, and copper from wastewater

Khue Anh Vo[a,b], Xiao Jun Xu[a,*], Tian Guo Li[a], Rui Hao Peng[a], Shu Li Liu[a], Xiu Lin Yue[a]

[a]*Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, Yunnan, China, Tel. +84 0905339749; email: khue_80@yahoo.com (K.A. Vo), Tel. +86 13577132038; emails: xuxiaojun88@sina.com (X.J. Xu), 550788873@qq.com (T.G. Li), pengruiha@163.com (R.H. Peng), 1203293826@qq.com (Sh.L. Liu), 304982971@qq.com (X.L. Yue)*
[b]*Faculty of Chemical Engineering, Tuy Hoa Industrial College, Tuy Hoa 620900, Phu Yen, Vietnam*

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ABSTRACT

Research on a new electrochemical method with iron electrodes and aluminum electrodes for removal of lead, zinc, and copper from wastewater was studied. Several parameters such as initial pH, hydraulic retention time, mass of Fe/C, applied voltage, and particle diameter of Fe/C were studied to achieve a high removal capacity. The results indicated that the new electrochemical method using aluminum electrodes or iron electrodes for removal efficiency of lead, zinc, and copper are very high. But the lifetime of aluminum electrodes is smaller than 2.44 times the lifetime of iron electrodes. The optimal condition of the new electrochemical method was achieved in two iron electrodes, an initial pH of 4–6, a hydraulic retention time of 75 min, a mass of Fe/C of 125 g, an applied voltage of 10 V, and a particle diameter of Fe/C of 20–27 mesh. At this optimal condition and the initial concentration of ions of 50 mg/L, the residual concentration of lead, zinc, and copper are 0.548, 0.886, and 0.588 mg/L, respectively. The treated wastewater continues the use of chemical coagulation method to adjust the solution pH value of 9. After all treatment processes have been completed, the effluent wastewater is very clear and its quality exceeds the direct discharge standard.

Keywords: New electrochemical method; Chemical coagulation method; Lead; Zinc; Copper

1. Introduction

Heavy metal ions such as lead, zinc, and copper are contained in industrial wastewater, which strongly affects human health and pollutes the environment [1]. In recent years, several treatment methods have been suggested for the removal of heavy metal ions from industrial wastewater. Physical methods for the removal of heavy metal ions have proven to be too expensive, as in the case of electrodialysis [2] and electrodeionization [3]. Chemical methods used for treatments are precipitation followed by lime, aluminum sulfate, and ferric chloride as coagulants, but has some disadvantages such as high costs of maintenance and problems of sludge handling. Biological methods are speed treatment slowly and unsuitable for treating large amounts of wastewater with a high concentration of heavy metal ions. At present, the most popular

*Corresponding author.

method for removal of heavy metal ions from wastewater is precipitation method by alkaline solutions. However, the treated wastewater by this method has some disadvantages such as the residual concentration of heavy metal ions is usually larger than 1 mg/L [4], the solution pH value is commonly larger than the discharge standard, large amounts of sludge are generated, the residual concentration of calcium ion is very large and the settling down of the particle precipitation in the solution is very slow, etc.

Recently, the electrocoagulation method is used extensively in industrial wastewater treatment. The electrocoagulation method has been successfully performed for decolorization treatment of dyes and remediation of the dye-house wastewaters [5], treatment of oil wastes [6], treatment of heavy metal bearing effluents [1], etc. Several studies about electrocoagulation method are summarized as follows as: Kamaraj et al. studied copper removal from wastewater by electrocoagulation process effect of alternating current (AC) and direct current (DC) [7]. The main objective of this study is to investigate the effects of AC and DC on the removal of copper from water using magnesium alloy as anode and cathode. The results showed that the optimum removal efficiency of copper is 97.8 and 97.2% for AC and DC, respectively. Kamaraj et al. studied 4-chloro-2-methylphenoxyacetic acid removal from wastewater by electrocoagulation method [8]. The results showed that the maximum removal efficiency of 83.72% was achieved with magnesium as the sacrificial anode at a current density of 0.10 A/dm^2 and pH of 7.0. Vasudevan et al. used electrocoagulation method for the simultaneous removal of mercury, lead, and nickel ions from water [9]. The results showed that the maximum removal efficiency was achieved for mercury, lead, and nickel with magnesium alloy as anode and galvanized iron as cathode at a current density of 0.15 A/dm^2 and pH of 7.0. Vasudevan et al. used electrocoagulation method for the removal of chromium from drinking water [10]. The results showed that the optimum removal efficiency of 98.2% was achieved using aluminum alloy anode at a current density of 0.2 A/dm^2, at a pH of 7.0. Vasudevan et al. studied cadmium removal from wastewater by electrocoagulation method with magnesium as anode and stainless steel as cathode [11]. The use of electrocoagulation method for removal of heavy metal ions from wastewater has many advantages such as simple operation, a hydraulic retention time of short, etc. However, this method also has many disadvantages such as energy consumption is large, large amounts of sludge are generated, cost of wastewater treatment is high, the optimal condition of initial pH is relatively high [9–11], etc.

In addition, recently the micro-electrolysis method also is used extensively in industrial wastewater treatment. The micro-electrolysis method has been successfully performed for improving the biodegradability before the bioprocess treatment [12], treatment of zinc and lead smelting wastewater [13], etc. The use of micro-electrolysis method for removal of heavy metal ions from wastewater has many advantages such as simple operation, non-use of electric power and cost of wastewater treatment of low, etc. However, this method also has many disadvantages such as low removal efficiency, speed slowly, easy clumping of Fe/C, etc. [14].

To address the above considerations, the study of a new method suitable for removal of heavy metal ions from the wastewater is necessary. In this paper, using a new electrochemical method for simultaneous removal of lead, zinc, and copper from wastewater was studied. This new electrochemical method is the combination of electrocoagulation, micro-electrolysis, and fluidized bed. Where the electrocoagulation method used iron electrodes and aluminum electrodes; the micro-electrolysis method used particles of Fe/C. The fluidized bed method was used to provide oxygen for the treatment system and to prevent the clumping of Fe/C, therefore, reduce the passivation problem of the particles of Fe/C [14].

Besides, in this study also used the new electrochemical method combined with the chemical coagulation method. The purpose of using chemical coagulation method is to enhance the coagulation of lead, zinc, and copper ions.

2. Materials and methods

2.1. Materials

$Pb(NO_3)_2$, $ZnSO_4$, $CuSO_4$, H_2SO_4, HNO_3, NaOH, and KCl were of analytical grade (Merck). Specifications of aluminum electrodes and iron electrodes are long 28 cm, wide 4.7 cm, and thick 1 mm. The particle of Fe/C bought at Weifang Yan Wal Yun Pu environmental technology company, China.

The equipment was used in the experiment include: self-made kit as Fig. 1, water velocity meter LZB-25, water pump AP 1600, *atomic absorption spectroscopy* AA240FS, machine transforms from AC to direct KGF50A/50V, and other equipment.

Where the volume of wastewater tank is 3.5 l; the volume of the electrolysis reaction tank is 0.66 l; two electrodes put parallel and spaced 4.5 cm; the particles of Fe/C were put in the space between two electrodes.

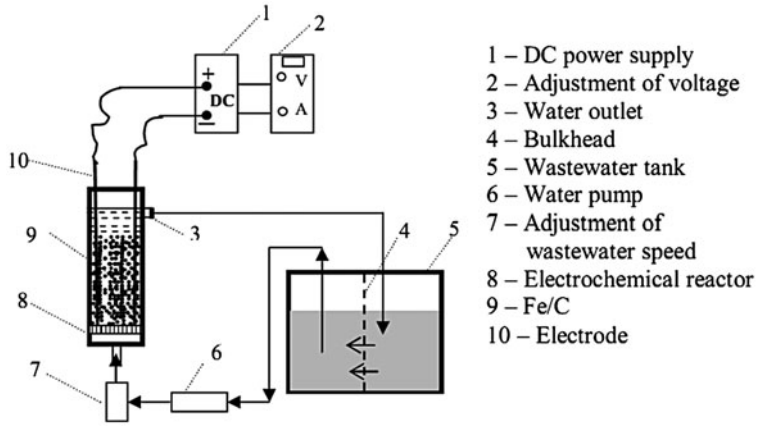

Fig. 1. Schematic of the new electrochemical method.

2.2. Methods

The concentration of lead, zinc, and copper ions are measured by *atomic absorption spectroscopy*. Concentration of Al^{3+} and Fe^{3+} are measured by the complex titration method. Iron consumption of the electrode is calculated by the mass method (because only the positive electrode corrosion [15,16]). Iron consumption of Fe/C is calculated from equation following:

$$m_{Fe(3)} = m_{Fe(1)} - m_{Fe(2)} \quad (1)$$

where $m_{Fe(1)}$—mass of iron is measured by the complex titration method (mg); $m_{Fe(2)}$—iron consumption of electrode (mg); $m_{Fe(3)}$—iron consumption of Fe/C (mg);

Energy consumption P is calculated from equation following [17]:

$$P = U \times I \times t \quad (2)$$

where P—energy consumption (Wh); U—applied voltage (V); I—current intensity (A); t—time (h).

By the orthogonal experiments, the study of the main factors influencing the efficiency of the treatment process, the factors and levels of experiments were shown in Table 1.

Where A—initial pH, B—hydraulic retention time (minute), C—mass of Fe/C (g), D—applied voltage (V) and E—particle diameter of Fe/C (mesh). Other factors of the experiment are fixed such as distance of two electrodes of 4.5 cm; wastewater speed of 260 l/h; initial concentration of lead, zinc, and copper ion of 50 mg/L; volume of a sample of 3 l.

Table 1
Arrangement of orthogonal experiment L_{16} (4^5)[a]

	Factor				
Level	*A*	*B*	*C*	*D*	*E*
1	3	45	75	5	14–17
2	4	60	100	10	18–19
3	5	75	125	15	20–27
4	6	90	150	20	28–34

[a]L_{16} (4^5) means 5 factors with 4 levels.

The experiments used aluminum electrodes which are added KCl of 1.5 g. Because the chloride salt added to the solution can prevent the formation of the alumina layer on the anode, therefore, reduce the passivation problem of the electrode [18].

To test the effect of initial concentration of lead, zinc, and copper on the ions removal efficiency of the new electrochemical method, a set of experiments were conducted by the orthogonal experiments, the factors and levels of experiments are shown in Table 2.

Table 2
Arrangement of orthogonal experiment L_9 (3^3)[a]

	Factor (mg/L)		
Level	Pb^{2+}	Zn^{2+}	Cu^{2+}
1	10	10	10
2	50	50	50
3	200	200	200

[a]L_9 (3^3) means 3 factors with 3 levels.

3. Results and discussion

3.1. Effect of experimental factors on energy consumption and removal efficiency of ions

The object of the experiment is the sample wastewater containing lead, zinc, and copper ions. Initial concentrations of these ions are 50 mg/L. Because the sample contains lead and sulfate ions, therefore, has a reaction following:

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \downarrow \quad K_s = 1.6 \times 10^{-8}\ \text{mol/L} \qquad (3)$$

$$K_s = \left[Pb^{2+}\right] \times \left[SO_4^{2-}\right]$$

$$\Rightarrow \left[Pb^{2+}\right] = 1.26 \times 10^{-4} M = 26.082\ \text{mg/L}$$

Thus, the solubility of $PbSO_4$ in pure water is 26.082 mg/L Pb^{2+}. Therefore, a solution containing lead, zinc, copper, and sulfate ions has appeared a part of the $PbSO_4$ precipitate.

In this section, the effect of experimental factors on energy consumption and removal efficiency of ions is examined by orthogonal experiments model. These factors and levels of experiments are shown in Table 1.

The experiments are conducted based on Table 1 and orthogonal design of L_{16} (4^5) [12], and then use the variance analysis method to analyze results. Experimental results were shown in Figs. 2–4.

From Fig. 2 noticed: effect of factor D (applied voltage) on energy consumption is largest. Therefore, we must be special attention to the factor D in choosing of the optimal condition for simultaneous removal of lead, zinc, and copper ions. Energy consumption by the use of aluminum electrodes is much higher than iron electrodes. Because the experiments used aluminum electrodes which are added KCl of 1.5 g, so the electrical conductivity of solutions is increased.

From Figs. 3 and 4 noticed: the new electrochemical method with two aluminum electrodes or two iron electrodes treated simultaneously of Pb^{2+}, Zn^{2+}, and Cu^{2+} for removal efficiency very high. In the same experimental conditions are the removal efficiency of $Pb^{2+} \approx Cu^{2+} > Zn^{2+}$. Factors and corresponding levels hardly affected the removal efficiency of lead and copper ions. But factors and corresponding levels affected on the removal efficiency of zinc ion very large.

The optimal condition for simultaneous removal of lead, zinc, and copper ions in the case of the new electrochemical method with two aluminum electrodes is selected based on Figs. 2 and 3. The results indicated that the optimal condition to achieve high performance and low energy consumption is: $A_2A_3A_4$, B_3, C_3, D_3, E_3 with an initial pH of 4–6, a hydraulic retention time of 75 min, a mass of Fe/C of 125 g, an applied voltage of 15 V and a particle diameter of Fe/C of 20–27 mesh, respectively.

The optimal condition for simultaneous removal of lead, zinc, and copper ions in the case of the new electrochemical method with two iron electrodes is selected based on Figs. 2 and 4. The results indicated that the optimal condition to achieve high performance and low energy consumption is: $A_2A_3A_4$, B_3, C_3, D_2, E_3 with an initial pH of 4–6, a hydraulic retention time of 75 min, a mass of Fe/C of 125 g, an applied voltage of 10 V and a particle diameter of Fe/C of 20–27 mesh, respectively.

Thus, the optimal conditions of the new electrochemical method using two aluminum electrodes and using two iron electrodes are quite similar. They only

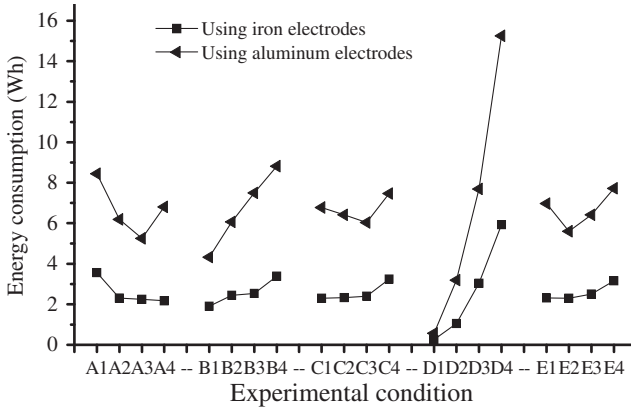

Fig. 2. Relationship between experimental conditions and energy consumption.

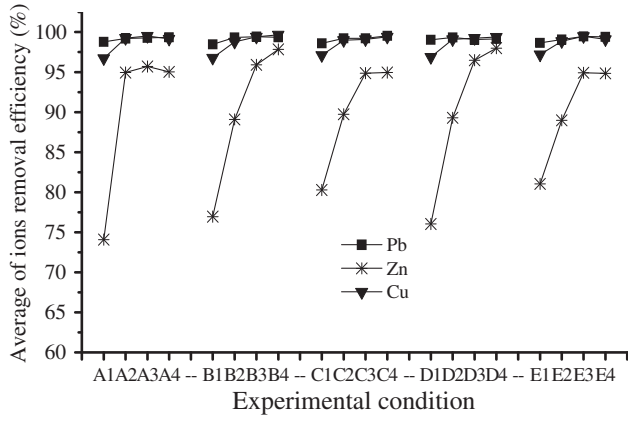

Fig. 3. The relationship between experimental conditions and removal efficiency of ion (using two aluminum electrodes).

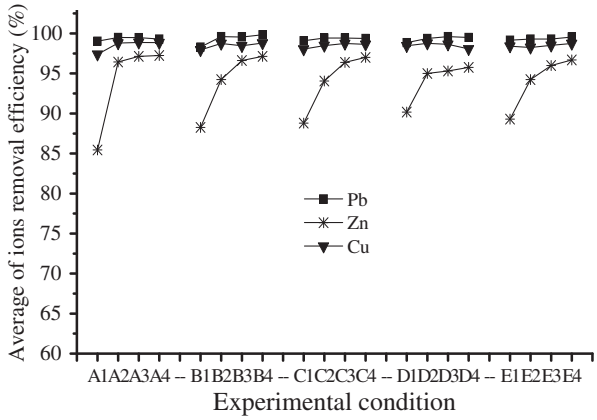

Fig. 4. The relationship between experimental conditions and removal efficiency of ions (using two iron electrodes).

differ in two points: using aluminum electrodes add KCl of 1.5 g, using iron electrodes don't add KCl; applied a voltage of the aluminum electrode of 15 V, applied voltage of the iron electrode of 10 V.

At these optimal conditions, the initial concentration of ions of 50 mg/L, the volume of the sample of 3 l and initial pH of 4, the results of the wastewater treatment process were shown as Table 3.

Table 3 was shown that the new electrochemical method with aluminum electrodes or iron electrodes for simultaneous removal of lead, zinc, and copper ions are very good. After the treatment process, the residual concentrations of Pb^{2+}, Zn^{2+}, and Cu^{2+} are smaller than the direct discharge standard of industrial wastewater.

Table 3 was also shown that energy consumption of the new electrochemical method with aluminum electrodes is larger than six times of iron electrodes. Sum of metal consumption of the new electrochemical method with aluminum electrodes is larger than 2.74 times of iron electrodes, therefore, mass of sludge of the new electrochemical method with iron electrodes is many smaller than aluminum electrodes.

Thus, cost of wastewater treatment by the new electrochemical method with aluminum electrodes is larger than iron electrodes.

3.2. The new electrochemical method using two iron electrodes combined with the chemical coagulation method

At the optimal condition of the new electrochemical method using two iron electrodes for simultaneous removal of lead, zinc, and copper from wastewater was achieved a good result. However, wastewater after treatment has the pH value of 5.11 and many solid *particles suspended in solution*. Therefore, wastewater after treatment by this new electrochemical method must continue using sodium hydroxide to adjust pH. The experimental result was shown in Table 4 and Fig. 5.

Table 4 was shown that the use of sodium hydroxide to adjust the solution pH value will enhance removal efficiency of lead, zinc, and copper ions. Specifically, the solution pH value is from 7 to 10, the residual concentration of lead is decreased. But the solution pH value is from 10 to 12, the residual concentration of lead is increased. Similarly, the solution pH value is from 7 to 9, the residual concentration of zinc is decreased. But the solution pH value is from 9 to 12, the residual concentration of zinc is increased. Because $Pb(OH)_2$ and $Zn(OH)_2$ are amphoteric hydroxides (see reaction Eqs. (4) and (5). The solution pH value is 8 or more, the residual concentration of copper is 0.000 mg/L.

$$Pb(OH)_2 \downarrow + 2OH^- \rightarrow Pb(OH)_4^{2-} \quad (4)$$

$$Zn(OH)_2 \downarrow + 2OH^- \rightarrow Zn(OH)_4^{2-} \quad (5)$$

Table 3
The results of the wastewater treatment by the new electrochemical method with two aluminum electrodes and two iron electrodes

The new electrochemical method	The solution pH value after treatment	Energy consumption (Wh)	Metal consumption (mg)			Residual concentration (mg/L)		
			Aluminum electrode	Iron electrode	Iron of Fe/C	Pb^{2+}	Zn^{2+}	Cu^{2+}
Two aluminum electrodes	7.03	7.50	409.2	0.0	675.7	0.064	0.156	0.030
Two iron electrodes	5.11	1.25	0.0	130.2	265.4	0.548	0.886	0.588

Table 4
The residual concentration of heavy metal ions is treated by the new electrochemical method using two iron electrodes combined with chemical coagulation

	pH					
Ion	7	8	9	10	11	12
Pb^{2+} (mg/L)	0.034	0.031	0.030	0.025	0.086	0.116
Zn^{2+} (mg/L)	0.200	0.100	0.012	0.014	0.207	0.350
Cu^{2+} (mg/L)	0.015	0.000	0.000	0.000	0.000	0.000

Fig. 5 was shown that the treated wastewater by the new electrochemical method had the solution pH value of 5.11, solid *particles suspended* and golden brown. Thus, it didn't meet qualify for discharge into the environment. When adjusting the solution pH value is from 7 to 12, the cleanliness of the solutions is increased. Specifically: in pH 7–8, the solutions have golden brown; in pH 9–12, the solutions are throughout. But the solution pH value of 10–12 is higher the discharge standards. Thus, the optimal condition of the chemical coagulation method is to adjust the solution pH value of 9. After all treatment processes have been completed, the residual concentration of lead, zinc, and copper ions are 0.030, 0.012, and 0.000 mg/L, respectively.

3.3. Current efficiency

The current efficiency is defined as the ratio of the actual electrode consumption to the theoretical value. It is an important parameter in the electrocoagulation process because it affects the lifetime of the electrode. So, the both values, theoretical and experimental, the consumed electrode are determined. The first one is calculated using Faraday's law [19–21]:

$$m_{Fe} = AIt/nF \quad (6)$$

where A—the molecular weight (g/mol); I—current intensity (A); t—time (s); F—Faraday's constant (96,500 C); n—the number of electrons corresponding to iron or aluminum oxidation.

In the case of the experiment with two iron electrodes was conducted in an initial pH of 4, a hydraulic retention time of 75 min, a mass of Fe/C of 125 g, an applied voltage of 10 V and a particle diameter of Fe/C of 20–27 mesh. The result was shown that both the actual electrode consumption and theoretical value are similar. Thus, the current efficiency is 100%. This result is similar with a reported in a recent study [15].

In the case of the experiment with two aluminum electrodes was conducted in an initial pH of 4, a hydraulic retention time of 75 min, a mass of Fe/C of 125 g, an applied voltage of 15 V and a particle diameter of Fe/C of 20–27 mesh. The result was shown that the current efficiency is 243.7%. Because besides electrochemical corrosion process, also happened chemical corrosion process at both anode and cathode of aluminum electrodes [14,17].

This result was shown that a lifetime of iron electrodes is larger than 2.44 times lifetime of aluminum

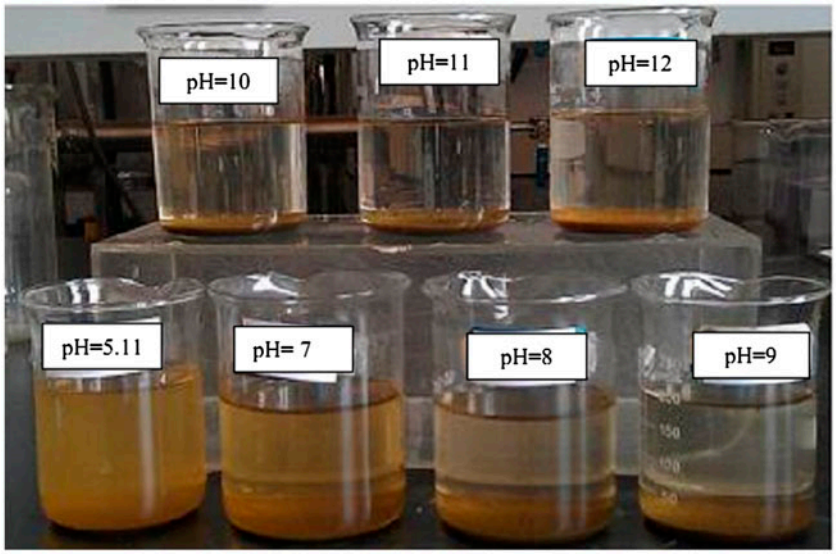

Fig. 5. The level of cleanliness of the samples after treatment.

electrodes. Thus, the new electrochemical method with iron electrodes simultaneous removal of lead, zinc, and copper from wastewater has a cost lower than aluminum electrodes.

3.4. Effect of initial concentrations of ions

To test the effect of initial concentration on the ions removal efficiency, a set of experiments was conducted by the orthogonal experiments. The factors and levels of experiments were shown in Table 2.

The experiments are conducted based on Table 2 and orthogonal design of L_9 (3^3) [19], and then use the variance analysis method to analyze results. Fig. 6 shows that experimental result:

These experiments were conducted on the optimal condition of the new electrochemical method with two iron electrodes, an initial pH of 4, a hydraulic retention time of 75 min, a mass of Fe/C of 125 g, an applied voltage of 10 V and the particle diameter of Fe/C of 20–27 mesh.

Fig. 6 was shown that the removal efficiency of lead and copper hardly depend on the initial concentration of lead, zinc, and copper. The initial concentrations of lead hardly affect the removal efficiency of zinc. When the initial concentration of zinc is 10–50 mg/L, the removal efficiency of zinc is slightly increased. But when the initial concentration of zinc is from 50 to 200 mg/L, the removal efficiency of zinc is significantly reduced. Worse zinc removal result was obtained with the increase in the copper concentration. These are probably because of the difference of removal mechanism of lead, zinc, and copper from wastewater. This mechanism will be presented in Section 3.5.

Thus, the new electrochemical method with two iron electrodes is suitable for treatment of Pb^{2+} and Cu^{2+} in the range of initial concentration of 200 mg/L. But this new electrochemical method is only suitable for treatment of Zn^{2+} in the range of initial concentration of 50 mg/L.

If the use of new electrochemical method combined with the chemical coagulation method can suitable for treatment of Pb^{2+}, Zn^{2+}, and Cu^{2+} within the large initial concentration.

3.5. Analysis of mechanism

3.5.1. Effect of external power on micro-electrolysis method

In this paper, using a new electrochemical method for simultaneous removal of lead, zinc, and copper from wastewater was studied. The new electrochemical method is the combination of electrocoagulation, micro-electrolysis, and fluidized bed. In this section, we examined the influence of the external power on the particles Fe/C. These effects were shown in Fig. 7.

Where (1) and (2) are two iron electrodes; (3)–(5), etc. are particles Fe/C).

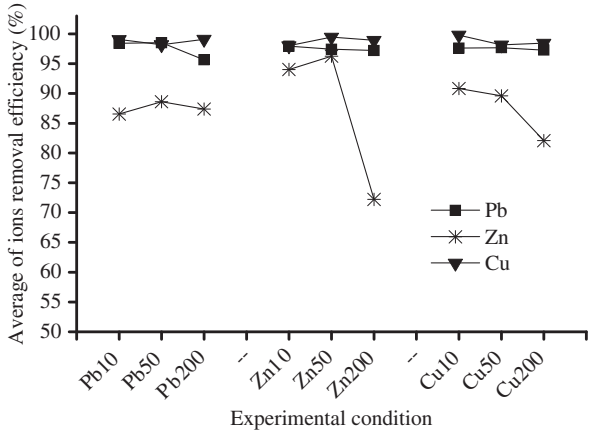

Fig. 6. Effect of initial concentration of Pb^{2+}, Zn^{2+}, and Cu^{2+} on the removal efficiency of Pb^{2+}, Zn^{2+}, and Cu^{2+}.

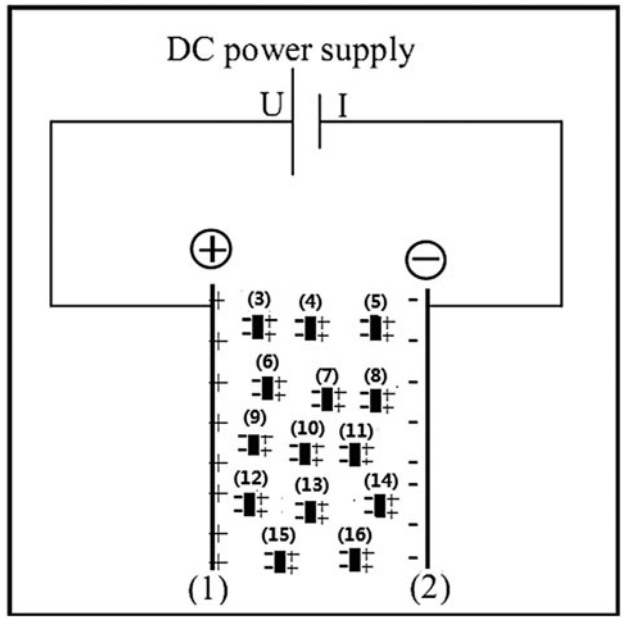

Fig. 7. Schematic of effect electric field on micro-electrolysis method.

Fig. 7 was shown that each particle Fe/C is an electric battery. Therefore, there are many electric batteries in the electrochemical reactor. When the electrochemical reactor does not use external power, each particle Fe/C is a battery electric, but its voltage is very small. If the electrochemical reactor uses external power, the voltage of the electric battery Fe/C will increase. In the electrochemical reactor, each particle Fe/C is a bipolar electrode [22]. The voltage of the bipolar electrode depends greatly on the voltage of the external power. If the voltage of the external power is large, the voltage of the bipolar electrode will be large and vice versa. Particle surface Fe/C toward the anode of the external power will be negatively charged. Particle surface Fe/C toward the cathode of external power will be positively charged. Thus, when the use of electrocoagulation method combined with micro-electrolysis method, particles Fe/C will corrode faster, oxidation in the anode surface and reduction in the cathode surface will happen faster.

3.5.2. Analysis surface by SEM and XPS

To analyze the mechanism of the new electrochemical method for simultaneous removal of lead, zinc, and copper from wastewater, an experiment was conducted in two iron electrodes, an initial pH of 4, a hydraulic retention time of 75 min, a mass of Fe/C of 125 g, an applied voltage of 10 V, a particle diameter of Fe/C of 20–27 mesh and the initial concentration of Pb^{2+}, Zn^{2+}, and Cu^{2+} of 50 mg/L. After the treatment process, particle Fe/C after reaction, particle Fe/C before reaction and sludge were dried at 50˚C for 10 h.

The surface shape of these solid phases was studied by SEM method (scanning electron microscopy). The results were shown in Fig. 8.

Fig. 8 was shown that there was a huge difference in the shape of the surface (a)–(c). This proves that the composition of matter on the surface of particles Fe/C before reaction, Fe/C after reaction and sludge had large differences. To analyze the surface composition of these solids, the next experiments were using the XPS method (X-ray photoelectron spectroscopy). The analysis result was shown in Table 5.

From Table 5 noticed: surface composition of the particles Fe/C before and after reaction has large differences. Before reaction, zinc has 0.82%, but after reaction zinc has 0%. Because in the particle Fe/C, Zn is the anode, therefore it is easily oxidized to generate Zn^{2+}.

$$Zn - 2e^- \rightarrow Zn^{2+}, \quad E^0(Zn^{2+}/Zn) = -0.76\ V \tag{7}$$

This demonstrates that Zn^{2+} cannot be reduced to generate zinc metal. Because E^0 (Zn^{2+}/Zn) is many smaller than E^0 (Fe^{2+}/Fe) (E^0 (Fe^{2+}/Fe) = −0.44 V).

The composition of copper and lead on the surface of Fe/C after reaction are higher than before reaction. This proves that lead and copper ions were reduced to generate lead and copper metal. But the reduction of copper ion into metal copper is better than the reducing of lead ion into metallic lead. Because E^0 (Cu^{2+}/Cu) is larger than E^0 (Pb^{2+}/Pb).

$$Pb^{2+} + 2e^- \rightarrow Pb\downarrow, \quad E^0(Pb^{2+}/Pb) = -0.13\ V \tag{8}$$

$$Cu^{2+} + 2e^- \rightarrow Cu\downarrow, \quad E^0(Cu^{2+}/Cu) = 0.34\ V \tag{9}$$

From Table 5 also noticed: in the precipitate composition contains zinc, copper, lead. This proves that the reaction between lead, zinc, and copper ions with

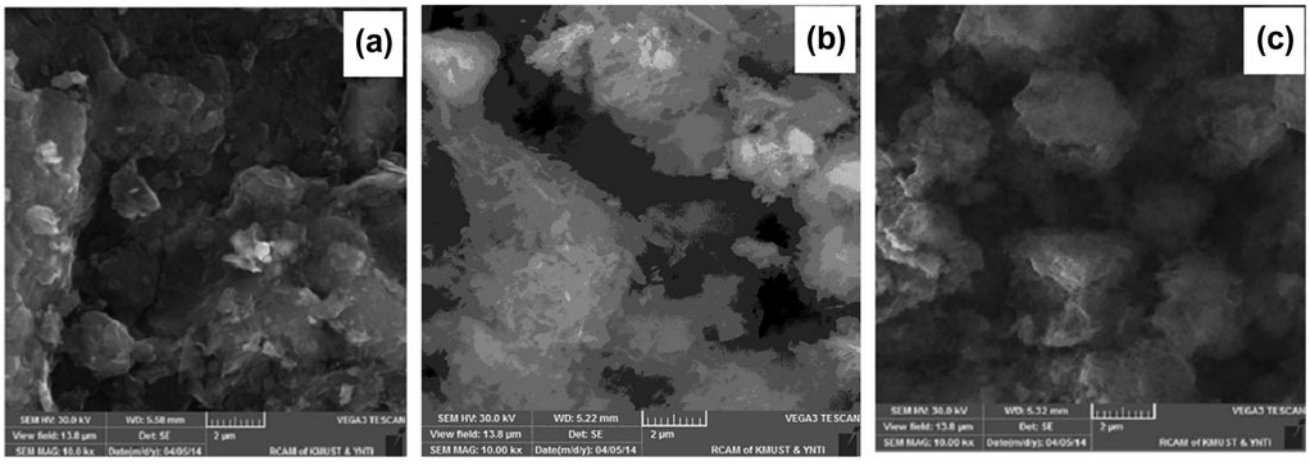

Fig. 8. The surface shapes: (a) particle Fe/C before reaction, (b) particle Fe/C after reaction, and (c) sludge.

Table 5
Characteristics of Fe/C before treatment, after treatment, and sludge

Atomic	Before treatment (%)	After treatment (%)	Sludge (%)
C 1s	74.22	16.05	11.51
O 1s	19.87	66.46	73.97
Fe $2p^3$	4.79	16.8	11.72
Zn $2p^3$	0.82	0.00	2.00
Cu $2p^3$	0.30	0.65	0.40
Pb 4f	0.00	0.04	0.40

hydroxides group formed the hydroxide precipitates such as $Pb(OH)^+$, $Pb(OH)_2$, $Cu(OH)_2$, $Zn(OH)_2$, etc.

Besides, a solution containing lead, zinc, copper, and sulfate ions will generate a part of the $PbSO_4$ precipitate.

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \downarrow \quad (10)$$

A schematic of the new electrochemical method for removal of lead, zinc, and copper ions from wastewater was shown in Fig. 9.

Where M is Pb, Zn, and Cu; M^{n+} is Pb^{2+}, Zn^{2+}, and Cu^{2+}.

Fig. 9 was shown that the mechanism of heavy metal ions removal was summarized as follows:

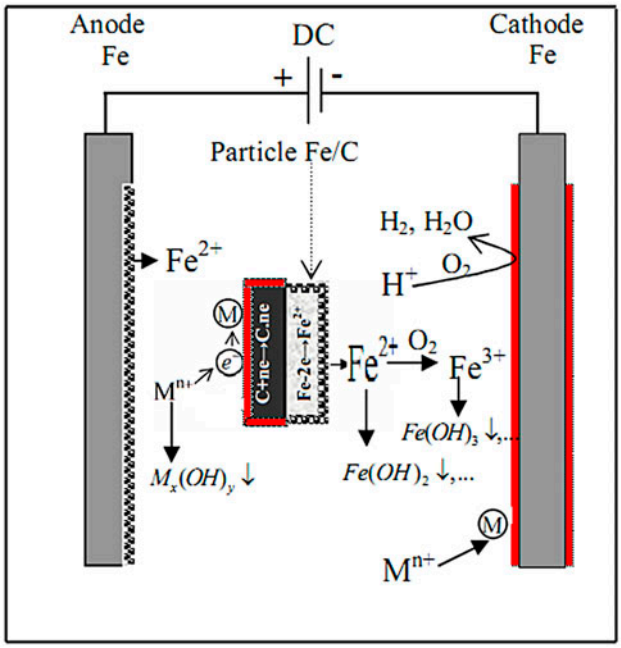

Fig. 9. Schematic of the mechanism for removal of Pb^{2+}, Zn^{2+}, and Cu^{2+} from wastewater by the new electrochemical method.

(1) At the anode: the half-cell reactions can be represented as oxidation in the anode surface (where anode is the positive electrode of iron and iron of particle Fe/C):

$$Fe \rightarrow Fe^{2+} + 2e^- \quad E^0(Fe^{2+}/Fe) = -0.44\ V \quad (11)$$

(2) At the cathode: the half-cell reactions can be represented as reduction in the cathode surface (where cathode is the negative electrode of iron and iron of particle Fe/C):

$$4H^+ + 4e^- \rightarrow 4[H] \rightarrow 2H_2 \uparrow \quad \text{(acidic)}$$
$$E^0(H^+/H_2) = 0.00\ V \quad (12)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{(acidic)}$$
$$E^0(O_2/H_2O) = 1.23\ V \quad (13)$$

$$M^{n+} + ne^- \rightarrow M \quad \text{(where M is Pb and Cu)} \quad (14)$$

(3) At the solution: occurring oxidation from Fe^{2+} into Fe^{3+} by oxygen.

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (15)$$

At the same time, the iron corrosion process attached to the increase in the pH of the solution (if the original wastewater is acidic) leading to the formation of hydroxide flocculation of Fe^{2+} and Fe^{3+} such as $Fe(OH)_2$, $Fe(OH)_3$, $Fe(OH)_4^-$, etc. These flocculations are co-precipitate and adsortion with the heavy metal ions. So, they can separate the heavy metal ions from wastewater.

Thus, the mechanism for removal of lead and copper from wastewater is due to the formation of hydroxide precipitates through co-precipitation with iron hydroxide, the reduction of Pb^{2+} and Cu^{2+} to generate lead and copper metal, the formation of $PbSO_4$ precipitate. The mechanism of removal zinc ion is the formation of hydroxide precipitates through co-precipitation with iron hydroxide.

4. Conclusions

The new electrochemical method using iron electrodes or aluminum electrodes for simultaneous removal of lead, zinc, and copper from wastewater are very good. But the cost of wastewater treatment by aluminum electrodes is higher than iron electrodes.

The new electrochemical method with iron electrodes combined with chemical flocculation is a safe and convenient route for effective removal of lead, zinc, and copper from wastewater. The optimal condition of this new electrochemical method for simultaneous removal of lead, zinc, and copper was achieved in two iron electrodes, an initial pH of 4–6, a hydraulic retention time of 75 min, a mass of Fe/C of 125 g, an applied voltage of 10 V and a particle diameter of Fe/C of 20–27 mesh. The treated wastewater was adjusted the solution pH value of 9, the residual concentration of lead, zinc, and copper are 0.030, 0.012, and 0.000 mg/L, respectively. After all treatment processes have been completed, the effluent wastewater is very clear and its quality exceeds the direct discharge standard.

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