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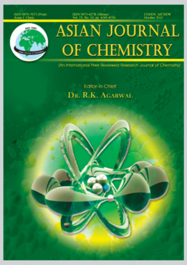

Removal and Recovery of Lead Ions from Wastewater of Lead-Acid Secondary Battery by a Hybrid Process Containing of Complexation-Ultrafiltration-Electrolysis

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A multi-stage process has been studied at pilot scale for the removal and recovery of lead from wastewater of a lead-acid secondary battery plant. In the treatment with a hybrid process of complexation-ultrafiltration-electrolysis, at first, Pb^{2+} ion is absorbed by polyacrylic acid and complexated into compounds. These compounds, which then become bigger than the pore size of the selected membrane in the ultrafiltration, can be retained and concentrated, whereas water of permeate is then purified from the feed solutions. Then Pb^{2+} ion is desorbed from the concentrated solution under the acid conditions. After second ultrafiltration process Pb^{2+} ion is separated from the polyacrylic acid. Finally the lead is recovered from the acid solution by electro-deposition.

Key Words: Lead ions, Wasterwater, Reuse, Polyacrylic acid, Complexating, Ultrafiltration.

INTRODUCTION

Lead is an extremely toxic pollutant that is currently being emitted mainly by low-level industrial sources. It is distributed globally through the groundwater, from where it precipitates onto the surface of the earth, enters aquatic organisms, accumulates in fish and finally affects the health of human being. Both the manufacture and recycling of lead acid batteries generate aqueous effluents containing low concentrations of Pb^{2+} species, for which the consent concentrations for permitted discharge to sewer are in the range from a few ppm down to zero, depending on the country, though the upper limits are likely to be decreased by environmental agencies in the future. For these reasons, the environmental regulation is becoming increasingly strict. For instance, the maximum permissible level of the Pb^{2+} ions in treated wastewater is 1 mg/L in China.

There are currently numerous effective methods to treat the wastewater containing Pb^{2+} ion, such as chemical precipitate, ion exchange resin and adsorption method, *etc*. But these methods in fact, whether Pb^{2+} ions of the feed solution was transformed to the precipitate or the form that was easily treated, was still a pollution metastasis, because these precipitate will be finally treated, usually be carried on landfill. But the risk of the Pb^{2+} ions to the environment still exists for a long time and the Pb^{2+} ions often causes the pollution of groundwater and surface water. In addition, these methods to treat the wastewater containing Pb^{2+} ions have some short comings in practically operation. For instance, the chemical precipitate can't removal all the Pb^{2+} ion in the wastewater because of the chemical equilibrium. The wastewater containing low concentrations of Pb^{2+} species can't be dealt with by these methods or the disposal of wastes is becoming increasingly expensive as costly environmental protection measures are imposed.

The hybrid process described in this paper allow this objective. Ultrafiltration, which is a membrane technology used to separate and concentrate species of high molecular weight present in the solution, is not able to removal ionic species such as metallic ions, because their pore radii are too small. In this coupling process, a fixation of these ions on macromolecular species is performed to increase their molecular weight. These compounds then become bigger than the pore sizes of selected membrane can be retained and flow out in the retentate whereas water of permeate is then purified from heavy metals. Consequently, the process is consisted of four steps: (1) complexation of a metal ion by a macro-ligand; (2) ultrafiltration of the complex; (3) ultrafiltration recovery the macro-ligand by acid decomposing; (4) recovery of the lead with electrolysis.

Some attempts at these processes had already been undertaken[1-3]. Ruey-Shin and Chwei-Huamm[4] demonstrated that it was possible to fix Cu^{2+} and Zn^{2+} using ultrafiltration by complexing them with weakly basic water soluble polymers[4]. Sanli and Asman also tried to remove Fe^{3+} by using polymer alginic acid[5]. It had also been demonstrated by Juang and Liang that copper and zinc solution could be concentrated using polyacrylic acid (PAA)[6]. But all membranes used in these processes were flat modules[7-11].

The former study[12] demonstrated the feasibility of the complexation-ultrafiltration process to reuse the wastewater. The better physico-chemical conditions: pH = 7.15, L = 1 and the best hydrodynamic conditions: ΔP = 200 KPa, VAM = 0.6 m s^{-1}, were also determined. Bsed on the former study, the purpose of this case would develop a more logical process containing of complexation-ultrafiltration-electrolysis (HPCUE) to reuse the heavy metal wastewater and recovery the metals. Therefore, collecting the wastewater containing lead ions from a lead-acid secondary battery plant, a pilot plant was assembled to evaluate this method in order to develop this process to a practical technology.

EXPERIMENTAL

The wastewater containing lead ions was collected from a lead-acid secondary battery plant. Table-1 shows the pollution index of the wastewater. The ultrafilteration membrane is a PVC hollow fiber membrane type having an effective area of 1 m^2 and molecular weight cut-off of 50000 Da. Polyacrylic acid (PAA) with an average molecular weight of 100000 Da, which must be pretreated before it is used, was chemical reagent used in the experiments. The pH was adjusted with 5 M H_2SO_4 and 5 M NaOH solutions and continuously monitored during each run.

TABLE-1
POLLUTION INDEX OF THE WASTEWATER OF A LEAD-ACID SECONDARY BATTERY PLANT

Index of the wastewater	Lead concentration (mg/L)	pH	COD (mg/L)	SS (mg/L)	Turbidity (NTU)
Value	1.9-4.1	2.4	38	2.4	3.0

Theory and experiments: The diagram of the pilot plant was shown in Fig. 1. Given L = 0.2, after the polyacrylic acid that had been pre-treated was poured into the wastewater tank, NaOH solution of 5 mol/L was added under stirring the wastewater till the pH value of the aqueous solution is *ca.* 7.0. Then, the complexation-ultrafiltration experiments was carried out under the condition of ΔP = 200KPa and VL = 0.6 m/s. 5 L concentrated solution extracted was added HCl solution of 5 mol/L till the pH value of it is 2. Then concentrated solution was steadiness-volume ultrafiltrated under the condition (ΔP = 200 Kpa, VL = 0.6 m/s).The feed solution (initial solution), which has a certain amount H_2SO_4 and can be used as eluant solution, was put into the wastewater storing pot constantly to maintain the volume of wastewater. In this process, the polyacrylic acid can be retained by membrane and separated from the Pb^{2+} ion. Because volume of the eluant solution in which the polyacrylic acid had been eliminated through the steadiness-volume ultrafiltration is much small, the device of electro-deposition recovery of lead of the lab scale can match the need. 2 L permeate solution was extracted to add in the traditional electric cell reactor with plate graphite electrode which has excellent characteristics and is cheap. Then the electro-deposition is carrying on under the condition of j = 56 A/m^2 which is proved to be the best parameter in the laboratory scale. After that the process of electro-deposition, recovery of lead and reuse of wastewater are achieved.

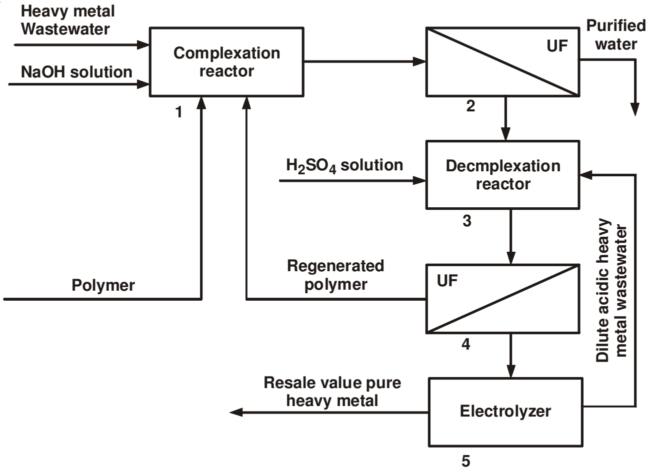

Fig. 1. Diagram of the principle of complexation-ultrafiltration-electrolysis hybrid process

Analysis: Lead(II) ion concentration of the feed and permeate solution were determined by atomic absorption spectroscopy (Philips PU9200X). COD, SS, turbudity and membrane flux rate in the permeate flux are measured to analysis. The effect of parameters, such as volume diluted factor (VDF), volume concentration factor (VCF) and time *etc.*, need to be measured to analysis.

RESULTS AND DISCUSSION

Change of the parameter in the permeate flux of long-term operation results with complexation-ultrafiltration: According to the pollution index of the wastewater quality of a lead-acid secondary battery plant shown as Table-1, COD and SS are relatively low, so the feed solution can carry on ultrafiltration directly without any pretreatment theoretically. But the Pb^{2+} ion can permeate membrane in ultrafiltration, so it is pretreated to bigger in the size, thus can be retained by membrane. Considering that the lead is relatively low in density of the wastewater, in order to get better getting rid of the result, the process of complexation-ultrafiltration should select polyacrylic acid adding amount smaller than the critical load value for use actually. Both retentate and permeate solutions were returned to the feed vessel to keep the concentration of the feed solution constant throughout the ultrafilteration experiments. Concentration change of the lead of the permeate solutions is shown as Fig. 2 in the coupling process of complexation-ultrafiltration which is circulated for a long time. It is evident that in 12 h in succession, the lead concentration of the permeate solutions measured is very low. The lead measuring line of the test equipment is 0.005 mg/L and the maximum concentration of the permeate solutions is 0.01 mg/L. It is obvious that after the coupling process of complexation-ultrafiltration, the rejection rate (R) of the Pb^{2+} ion can reach 100 % nearly. Not only the concentration of the Pb^{2+} ion is extremely low, but also the attenuation of membrane flux value is not remarkable (Fig. 3). In beginning 4 h, the membrane flux value drops very fast, but steady in 80 L/m^2 shortly. It is obvious that the wastewater of the lead-acid battery plant free from contamination to the ultrafiltration membrane and will not cause the constant attenuation of the flux. The reason may be that the concentration of the Pb^{2+} ion is low in the wastewater

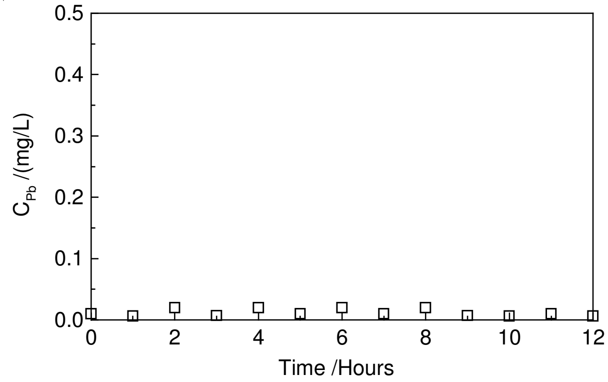

Fig. 2. Lead concentration in the permeate flux of long-term operation results with complexation-ultrafiltration coupling process

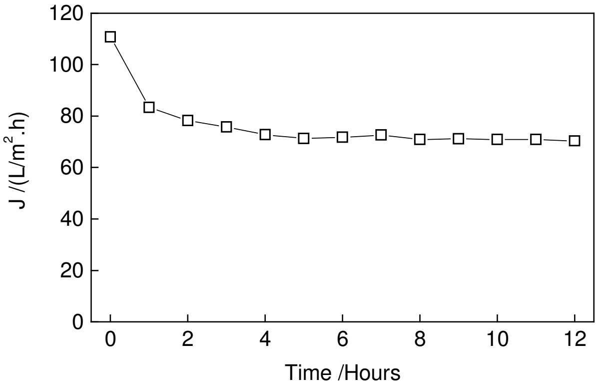

Fig. 3. Permeate flux of long-term operation results with complexation-ultrafiltration coupling process

of the lead-acid battery plant and the load of the ultrafiltration membrane is relatively small.

It can be found out from Figs. 4 and 5 that COD and turbidity of the permeate solutions much slow, COD $\leq$ 10 mg/L, turbidity $\leq$ 3 NTU, but SS = 0 mg/L. And within running time entirely investigating, these parameters of the permeate solutions are all more invariable. There is no obvious fluctuation and the quality of the permeate solutions is good and steady.

But the course of the wastewater treatment is a course of concentrating constantly in practice. The effect of volume concentration factor on J and R during the process of concentrating constantly is shown as Figs. 6 and 7. It can be seen from Fig. 6 that though volume concentration factor is up to 500 in test, the complexation-ultrafiltration remains higher R to the Pb^{2+} ion in the course of concentration (the lead in the permeate solution is extremely low in concentration). Volumetric concentration factor (VCF) has no effect on R of the lead ion (Fig. 6 show). The theory of the polyacrylic acid coupling process of complexation-ultrafiltration that, under certain physical-chemistry conditions, so long as the Pb^{2+} ion turns into the steady complex compound with polyacrylic acid, the ultrafiltration membrane can retain it is proved again. Because of the concentration of the wastewater rising constantly, the infiltration press of the solution rising and membrane pollution increasing in the course of concentration, the flux of membrane is dropping constantly. It is shown in Fig. 7 that The J reduces constantly while the volume concentration factor increases in the course of concentration. It is obvious that the max of volume concentration factor having been attained should be determined by the final flux of membrane. Considered from the economy that is operated, it is the better that the flux of membrane should be the larger, but the larger flux of membrane means little volume concentration factor. Thus the Pb^{2+} ion concentration of the solution which need be electrolyzed is too low. It is essential to deal with the contradiction of volume concentration factor and J correctly in treetment of the wastewater. Through numerous experiments, the volume concentration factor is confirmed as 400 and J at this moment is 20 L/m^2 h. However the Pb^{2+} ion concentration have reached about 800 mg/L in the waste water. It means that there is 99.75 % of the wastewater is retrieved and only 0.25 % of the wastewater becomes

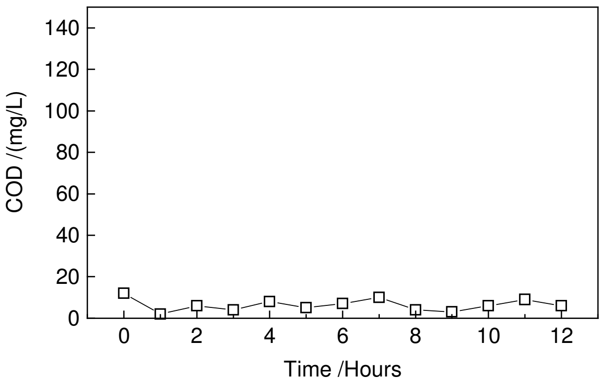

Fig. 4. COD in the permeate flux of long-term operation results with complexation-ultrafiltration coupling process

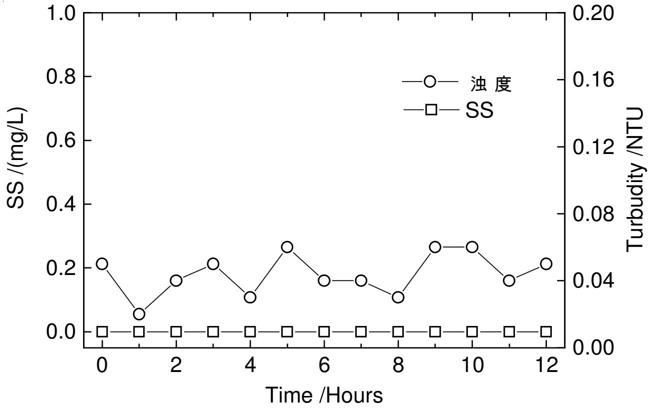

Fig. 5. SS and turbidity in the permeate flux of long-term operation results with complexation-ultrafiltration coupling process

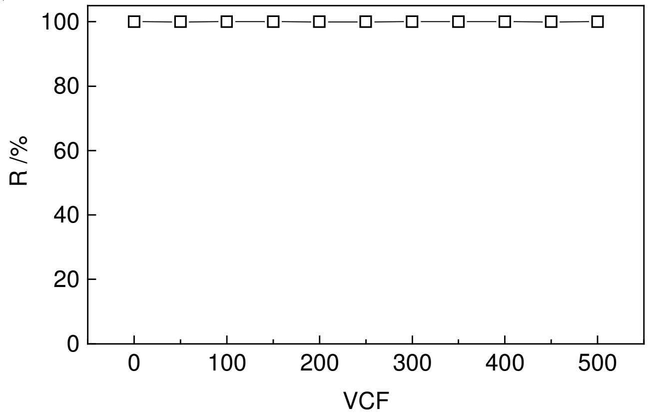

Fig. 6. Effect of volume concentration factor (VCF) on retention efficiency of Pb^{2+} with complexation-ultrafiltration coupling process

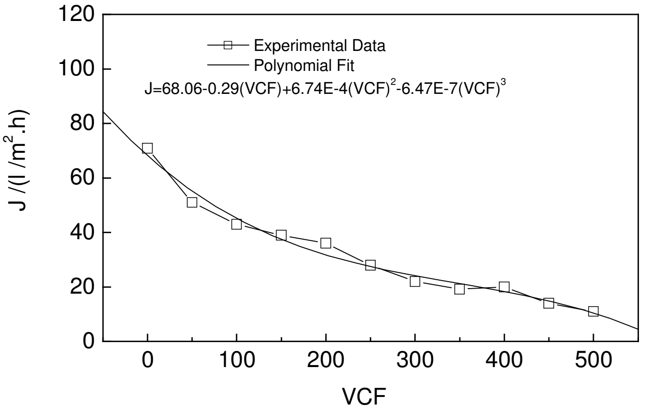

Fig. 7. Effect of volume concentration factor (VCF) on permeate flux of Pb with complexation-ultrafiltration coupling precess

concentrated solution which needs further treatment. Moreover the lead content of the wastewater of the lead-acid battery plant is relatively low, higher volume concentration factor is easily received. That makes for recovery of the lead in the process of electricity-deposit subsequently and retrieves more wastewater at the same time.

Effect of volume diluted factor in resolve acidly lead-polyacrylic acid compound and recovery of polyacrylic acid: The result of the test is shown as Table-2. According to the data of Table-2, Figs. 8 and 9 are obtained by drawing up the test data with the formations as follows:

$$C_R = C_0e^{-VDF(1-R)} \qquad 1—(1)$$

$$Y = e^{-VDF(1-R)} \qquad 1—(2)$$

$$X = 1-Y = 1-e^{-VDF(1-R)} \qquad 1—(3)$$

TABLE-2
EXPERIMENTAL RESULTS OF POLYACRYLIC ACID (PAA) RECOVERY EFFICIENCY AND Pb REMOVAL EFFICIENCY WITH VOLUME DILUTED FACTOR (VDF) FOR CONCENTRATED SOLUTIONS OF COMPLEXATION-ULTRAFILTRATION COUPLING PROCESS

VDF	V_P (L)	PAA		Pb	
		C_R (mg/L)	Y (%)	C_P (mg/L)	X (%)
0	0	3900	–	760.6	–
1	5	3760	96.4	270.3	35.6
2	10	3693	94.7	204.6	62.4
3	15	3650	93.6	89.1	74.1

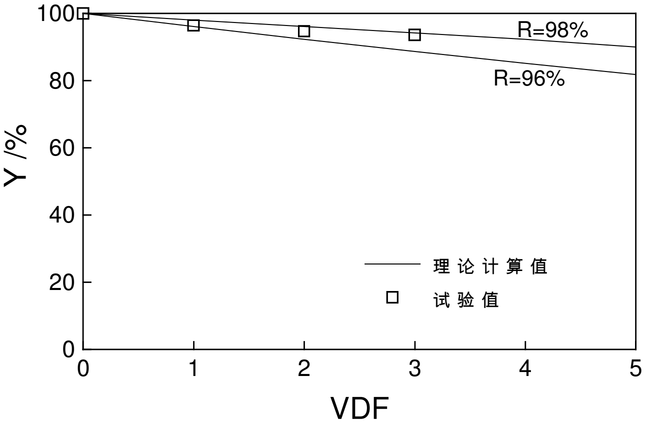

Fig. 8. Effect of volume diluted factor (VDF) on polyacrylic acid recovery efficiency for concentrated lead-polyacrylic acid solution by continuous diafiltration

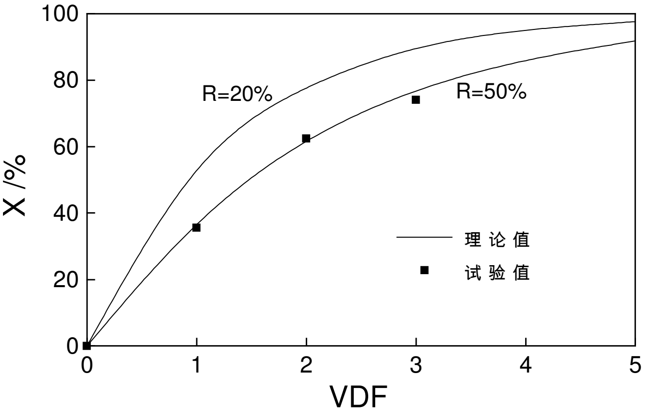

Fig. 9. Effect of volume diluted factor (VDF) on lead removal efficiency for concentrated lead-polyacrylic acid solution by continuous diafiltration

Fig. 8 shows that the volume dilute factor (VDF) rises, namely the volume of the permeate solution rising, the rate of recovery of polyacrylic acid is reduced gradually. Test data are more unanimous with the result of calculation of the rate of recovery of the theory when R = 98 %. It is obvious that the loss of polyacrylic acid is not serious. When the VDF = 3, there is 6.4 % of the polyacrylic acid penetrate the permeate solution. It is found that the loss of polyacrylic acid relates to pH and concentration. When pH < 6, the polyacrylic acid may penetrate ultrofiltration membrane; but when pH > 6, the R to polyacrylic acid is 100 %. Meanwhile, the higher the concentration of the polyacrylic acid is, the more the polyacrylic acid which penetrate membrane is. It can be seen that pH is another factor of restricting volume concentration factor in the couple process of complexation-ultrafiltration. The rising volume concentration factor not only makes the flux of membrane drop, but also makes the loss of polyacrylic acid increase in the course of resolve acidly lead-polyacrylic acid compound and recovery of polyacrylic acid.

Fig. 9 shown at the same time that the total rate of getting rid of lead is increasing constantly in the concentration along with the volume diluted factor rising during recovery of polyacrylic acid. The bigger the affinity of Pb^{2+} ion and polyacrylic acid is and the higher the concentration of polyacrylic acid is, the lower the getting rid of rate of lead is in the process of steadiness-volume ultrafiltration. Under this experimental condition, the concentration of the Pb^{2+} ion is 760 mg/L but that of polyacrylic acid is 3900 mg/L. So even pH = 2, the ultrafiltration membrane stills have 50 % R to the polyacrylic acid because polyacrylic acid and Pb^{2+} ion have better affinity. Even so, the concentration of the Pb^{2+} ion in eluant solution is still high as Table-2 shown. It can be calculated separately out according to the data of the Table-2 in different volume diluted factor:

Volume diluted factor = 2 concentration of Pb^{2+} ion in the take-off liquid C = 237.48 mg/L

Volume diluted factor = 3 concentration of Pb^{2+} ion in the take-off liquid C = 188.04 mg/L

It is obvious that total of getting rid of lead increases along with the volume diluted factor rising, but concentration of Pb^{2+} ion in the eluant solution is gradually low. Concentration of Pb^{2+} ion in the eluant solution having being too low will cause the low efficiency of the electric current while the electricity-deposit subsequently. So volume diluted factor = 3 is adopted. At this moment the concentrated solution has still 25.9 % of lead which concentration is 196.5 mg/L. The polyacrylic acid is recycled to the wastewater and continue to concentrate to make the total rate of recovery increase. The concentration of Pb^{2+} ion in wastewater of the lead-acid battery plant is relatively low so wastewater that need to deal with finally only have 0.25 % of original wastewater.

Effect of deposition time on lead concentration: It can be found (Fig. 10) that concentration of Pb^{2+} ion in the electrolytic liquid is falling constantly accompanied with the electricity-deposition and it drops very fast in beginning 30 min. Subsequently, because it is relatively low in the electrolytic liquid and the efficiency of the electric current is lower, the change of it is largo. But the lead can't have been measured in the electrolytic liquid after 50 min. The electric current efficiency of the electrolytic and electric energy consumed are 15 % and 21.8 KW h/kg Pb, respectively in 50 min. It is obvious that when efficiency of the electric current is low, electric energy consumed is great. According to whole course, the Pb^{2+} ion in wastewater has been concentrated from 2 mg/L to 188.04 mg/L in the concentration and retrieved in metal form.

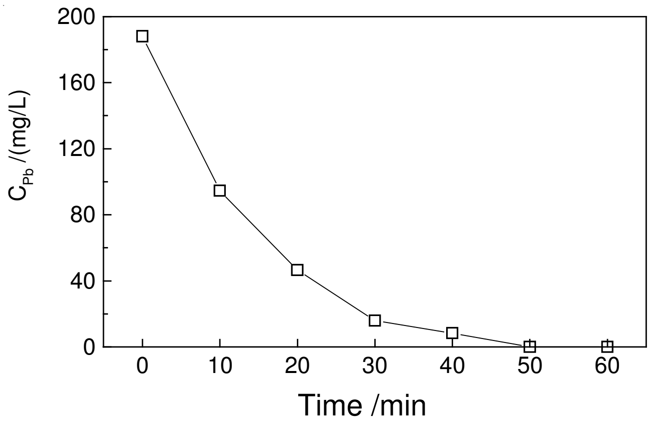

Fig. 10. Effect of deposition time on heavy metal concentration

Conclusion

Because of limit of the concentration and volume of the water sample in the lab scale, the volume concentration factor is only up to about 20, but the volume concentration factor is up to 400 in the pilot scale. Only 0.25 % of the concentrated solution needs dealing with. The complexation-ultrafiltration-electrolysis hybrid process (HPCUE) was a promising technique applied to the removal and recovery of lead from wastewater of a lead-acid secondary battery plant After fixing the better physicochemical conditions (pH = 7.0, L = 0.2) and the best hydrodynamic conditions(ΔP = 200 KPa, VL = 0.6 m s^{-1}) a constant R of 100 % nearly was obtained until the volume concentration factor was up to 400 after the process of complexation-ultrafiltration. Under the conditions (pH = 2, volume diluted factor = 3), nearly 93 % polyacrylic acid was obtained and 75 % Pb^{2+} ion come into the permeate solution in the recovery of polyacrylic acid. In the process of electro-deposition recovery of lead, all the Pb^{2+} ion is retrieved in metal form while electrical current density j = 56/m^2 in a hour. Efficiency of the electric current and electric energy consumed are 15 % and 21.8 KW h/kg Pb, respectively. The quality of the water the final permeate solution is fine and can reach demand to use as backwater after the treatment of this process. The pilot-scale test can offer project datum and design considerations for the fact that the industrialization of this course is used.

List of symbols

C_0	Concentration of initial feed solution (mg/L)
C_P	Concentration of permeate solution (mg/L)
C_R	Concentration of retentate solution (mg/L)
j	Current density (A/m^2)
J	Membrane flux (L/m^2 h)
L	Polyacrylic acid-Lead loading rate [g(lead)/g (PAA)]
PAA	Polyacrylic acid
PVC	Polyvinyl chloride
R	Rejection rate (%)
VCF	Volumetric concentration factor (%)
VDF	Volumetric dilution factor (%)
VL	Tangential linear velocity (m/s)
VP	Volume of permeate solution (L)
VR	Volume of concentrated solution (L)
t	Time
X	Removal efficiency of lead
Y	Recovery deficiency of polyacrylic acid

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