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Recovery of cobalt from spent lithium ion batteries using sulphuric acid leaching followed by solid-liquid separation and solvent extraction

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Abstract

This article adopt the method of hydrometallurgy to recycle the precious metal cobalt in spent lithium ion batteries (LIBs). The best experimental condition of leaching cobalt ions in sulphuric acid-hydrogen peroxide system is studied. The best leaching operation condition is that the concentration of the H₂SO₄ is 3.0 mol L⁻¹, liquid-solid ratio is 7:1 and hydrogen peroxide dosage is 1.6 mL g⁻¹ at 2.5 h under 70 °C. Using the extraction characteristics of D2EHPA (di-(2-ethylhexyl) phosphoric acid) and PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) for specific ion in different pH value leaching solution, the best experiment conditions are find that D2EHPA and PC-88A saponification rate are 20% and 30% respectively, the sulfonated kerosene volume accounted 70%, oil-water (O/A) ratio is 1:1, the extraction time is 10 mins. Twice extractions is applied, once extraction is take at pH 2.70 and secondary extraction is operated at pH 2.60 using D2EHPA to remove copper and manganese ions. After extraction operation, PC-88A is used to further extract the leaching solution and maintain pH at 4.25, so that cobalt and nickel ions are effectively separated, then cobalt ion is separated by oxalic acid, cobalt oxalate is obtained, and the purity of cobalt is up to 99.50%.

Keywords: Spent lithium-ion batteries; Recycling; Cobalt; Leaching; Extraction

1. Introduction

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The demand for sustainable and clean energy is becoming more and more critical owing to the emergence of applications in many new types of electronic devices currently available.¹ The world's major countries and regions of powder with incentives, vigorously promote the electric car, increase the intensity of power battery research especially lithium-ion batteries (LIBs).² Compared with lead-acid batteries, nickel cadmium battery and nickel metal hydride batteries, lithium ion battery presents advantages of most superior performances such as high working voltage, large energy density, no memory effect, low self-discharge rate and long cycle life, etc, thus it is widely used in consumer electronics. Owing to the constant introduction of new technologies which result in the shorter use of electronic products cycle lifespans, the spent LIBs have mushroomed in recent years.³⁻⁵

At present, the treatment methods of spent LIBs mainly includes incineration, landfill, and recycling. If unsuitable disposal of these batteries were carried on, serious environmental problems were generated due to their hazardous constituents including heavy metals and electrolytes. Cobalt contained spent LIBs is a highly toxic metal which could cause cancer owing to strong permeability. The price of cobalt has increased significantly in recent years,⁶ but content of cobalt in LIBs is up to 5%-20%, which is far beyond of average ore. So the effective recycling does not only reduce the production cost but also protect the environment.⁷⁻⁸

In order to efficiently recover the cobalt metal from the cathode materials, various physical and chemical methods have been reported,⁹⁻¹⁴ the most common recover processes include prometallurgy,¹⁵ hydrometallurgy,¹⁶ and biometallurgy.¹⁷

The recovery of cobalt ions was employed by hydrometallurgy process because of the high rate of recovery, low energy consumption and decrease the generation of waste water and gas. Hydrometallurgy process including crushing, dismantling, sieving, and leaching, solvent extraction, chemical precipitation and electrochemistry.¹⁸ Hydrometallurgy is considered as a good recycling process for the recovery of spent LIBs; cobalt, lithium and other metal ions are easily leached from spent LIBs using inorganic acid as leached agents such as HCl, HNO₃, and H₂SO₄.¹⁹⁻²¹ And with extra adding reducing agents hydrogen peroxide (H₂O₂), so as to accelerate the leaching

process of metal ions.

Up to now, a large number of methods used to recover metals from leaching liquor of spent LIBs are proposed.²²⁻²³ According to the relevant research, the main techniques are following listed in Table 1.²⁴⁻²⁷ However, the important drawback of the above techniques is the low purity of the cobalt compounds. Therefore, it is urgent to exploit new recovery processes to meet the demand of metals recycling from the already complicated waste stream.²⁸⁻²⁹

Solvent extraction has been widely used for the recovery and separation of metals from the leach liquor.³⁰ In order to obtain high purity metals concentrates, solvent extraction is more attention, which appears to satisfying the requirements of performance and economics.

In the current study, recycling of components in spent LIBs is accounted in the hydrometallurgical process. The experiment focused on the extraction and purification of cobalt ion in leaching liquor of spent LIBs. H_2SO_4 was employed to leaching agent, with H_2O_2 as reducing agent. The effect of leaching conditions such as temperature, time, concentration of the H_2SO_4 , liquid-solid ratio and H_2O_2 dosage on efficiency was determined. And the orthogonal experiment was designed to examine the relationship between the factors and the optimal experimental conditions. Solvent extraction process of experiments has been developed to preliminarily and selectively remove manganese and copper from the leach liquor using D2EHPA. Subsequently, the cobalt can be selectively separated from the liquid phase containing cobalt and nickel using PC-88A.

2. Experimental

2.1. Materials and reagents

Spent LIBs were supplied by the ChangHong Co., Ltd. (Mianyang, China). and the cathode material was obtained from spent LIBs after pretreatment (Detailed description of the next section). Sulfuric acid (H_2SO_4) were tested as the leaching agents. Hydrogen peroxide (H_2O_2 30%) was used as additional reductant. For the extraction tests, di-(2-ethylhexyl) phosphoric acid (D2EHPA, 95.7% in purity) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A, 95% in purity) was

used as extractant agent, and these were saponified by Sodium hydroxide solution (10 mol L⁻¹). Low boiling point sulfonated kerosene (180-270 °C) was used as diluents and tri-n-butylphosphate (TBP, 96.8% in purity) was used as the phase modifier. In the precipitation step, oxalate (analytical grade) was used as precipitating agent.

All other solutions were prepared with ultrapure water and all chemical reagents were used without further purification and supplied by Chengdu Kelong Chemical Reagent Co., Ltd., China.

2.2. Preparation of LIBs cathode material

Batteries used in the experiment of cathode material from ChangHong electric Co., Ltd. (Mianyang, China). Firstly, LIBs was crushed using wet crushing; secondly, large particle were removed using vibrating screen; then the residue was dried at 105 °C for 2 h, and the images of the residue was shown in Fig. 1a.

2.3. Analytical methods

The spent LIBs cathode material and precipitation of cobalt oxalate was carried out with an X-ray Diffractometer (XRD panalytical Axios, Cu-Ka). The X-ray fluorescence (XRF panalytical Axios, Rh-Ka) has been used for spent LIBs cathode material. Scanning electron microscopy (SEM) microphotographs and the elementary composition analysis were obtained with a Carl Zeiss Ultra 55 field emission SEM (FE-SEM) equipped with an energy-dispersive X-ray (EDX) detector operating at 15 kV. The pH values of the aqueous solutions were measured with a pH/mV meter (Model PHS-3C+) and Fourier transform infrared (FT-IR, Nicolet-5700, PerkinElmer Instruments Corporation) was employed for the identification of the relevant vibrational characteristic bands of cobalt oxalate. The metal ions were performed by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP, AES-ICAP6500) which is very accurate with a high sensitivity to estimate the rare element. In this research, thermal analyses for the spent LIBs powder were performed using a Thermo-gravimetric Analyzer (TG, Q500 TGA USA) in an nitrogen atmosphere from 30 to 1000 °C at a heating rate of 10 °C min⁻¹.

2.4. Metal leaching

H₂SO₄ and H₂O₂ (30%) were used to leach the Co²⁺ from spent LiBs; the

experiment was carried out at a setting temperature with a reflux condenser, and the Co^{2+} leaching process is optimized by orthogonal experimental conditions $L_{16}(4^5)$. Generally, the leaching process was mainly influenced by the concentration of H_2SO_4 , temperature, leaching reaction time and the dosage of H_2SO_4 solid-to-liquid ratio (S:L), H_2O_2 dosage. Firstly, the diluted H_2SO_4 solution was added into the three flask; then the spent LIBs cathode material (30.0000 g) was putted in the diluted H_2SO_4 solution; lastly, H_2O_2 was dropped into the mixed solution with a constant magnetic stirrer. After the reaction, the filter residue was filtered, washed and the leaching filtrate was collected constant volume to 1000 mL. The concentration of cobalt and other metal ions were detected. Factors and levels of orthogonal experiment were listed in Table 2.

2.5. The effect of initial pH on concentration of metal ions in leaching solution

The appropriate pH value of 800mL leaching solution was adjusted by adding 2.0 mol L^{-1} sodium hydroxide solution and maintained 10 mins, the initial adjustment in the process of pH will have a small amount of floc produced. The purified solution and some mico precipitate were separated by filtration. The content of each metal in the filtrate was measured.

2.6. Solvent extraction

Hydrometallurgy is the main method to recycle cobalt metal from spent LIBs, and the leaching of cobalt ions from cathodic material is carried out by H_2SO_4 - H_2O_2 systems. However, Leaching liquors not only contains cobalt ions but also included nickel, copper and manganese metal ions. It is extremely difficult to obtain pure cobalt compounds from these complicated leaching liquors, because nickel, manganese, copper possess similar physico-chemical properties. A clever method to obtain the high purity of cobalt is determined by a kind of extraction agent which could separate the cobalt and other metal ions efficiently. To our knowledge, it has not been reported that there are exist a selective extraction agent which could extract cobalt ion efficiently and make the other metal ions be separated. Therefore, it is the key to obtain high purity cobalt by using a combination of several extraction agents.

The literature has been reported the cobalt-nickel separation factors from H_2SO_4

media using phosphoric, phosphonic and phosphinic acids. The separation ability of cobalt and nickel increases in the order phosphinic > phosphonic > phosphoric acid due to the increasing stabilisation of tetrahedral coordination compound of cobalt with the extractant in the organic phase, because the tetrahedral compound is more lipophilic than the octahedral one.³¹⁻³³ The organophosphorus extractants D2EHPA and PC-88A in H₂SO₄ medium possess excellent extraction characteristics for metal manganese, copper and nickel, respectively.³⁴⁻³⁵ However, keeping the constant of pH value is essential in liquid before and after extraction process, because the extraction abilities of D2EHPA and PC-88A are closely related to the liquid of pH. In order to keep pH stable, D2EHPA and PC-88A were saponified by 10 mol L⁻¹ sodium hydroxide solution. The saponification ratio of D2EHPA and PC-88A in the test was 20% and 30% (mole percent), respectively. The sulfonated kerosene was used as the diluent (Dilution is implemented by mixing 30 vol.% D2EHPA or PC-88A with 70 vol.% sulfonated kerosene) and 5 vol.% tri-n-butylphosphate was used as the modification of phase separating agent. Batch contacts with phase ratio O/A=1:1 (100 mL volumes of leaching aqueous and 100 mL modulated extractant solution), extraction and separation were strictly constrained at room temperature in a 500 mL separatory funnel by manually shaking about 15 mins, then rest for 10 mins, the aqueous phase was taken for analysis after phase separation. The pH of the aqueous solution was adjusted to the desired value by adding dilute H₂SO₄ or NaOH before equilibration. Finally, the acidity of the aqueous phase was tested by using a digital pH meter. The concentration of metal in filter liquor was determined by ICP-AES. The recovery rate of the extraction fraction can be measured by the ratio of the cobalt ion concentration in the final extraction reagent PC-88A to the cobalt ion concentration in the initial leaching solution. The main route comprises step extraction process was shown in Fig. 2.

2.7. Chemical precipitation of cobalt oxalate

In order to precipitate precious metals cobalt ion which obtained via extraction process, the chemical precipitation method was applied. The cobalt was precipitated from the strip liquor of PC-88A extractant by addition of excess 0.5 mol L⁻¹ oxalate.

In addition, the solubility integral of copper, manganese, nickel and cobalt are 4.4×10^{-10} , 1.7×10^{-7} , 4.0×10^{-10} and 6.3×10^{-6} , respectively, in oxalic acid solution.³⁶ The solubility of cobalt ion product is larger and easier to form precipitation compared with other metal ions. What's more, the concentration of cobalt ion is far higher than that of other metal ions in extractant PC-88A phase, presenting the cobalt ion is precipitated by oxalate more easily and can realize efficient separation among other ions. The precipitating process could be expressed with the chemical reaction equation: $Co_{(aq)}^{2+} + C_2O_{4(aq)}^{2-} + 2H_2O \Rightarrow CoC_2O_4 \cdot 2H_2O_{(s)}$. After filtered and washed, the precipitated cobalt oxalate was obtained and then characterized by IR, XRD and ICP.

3. Results and Discussion

3.1. Characterization of the spent LIBs cathode material composition

The spent LIBs cathode material of XRD is shown in Fig. 3b. The result is clear that the strong diffraction intensity of peaks appeared at 2θ of 26.50° , the peak at 26.50° indicated that the main composition of cathode materials was graphite with integrated graphite layered structure. it can be noted that the graphite materials basically remain good crystallinity and the complete layer structure.³⁷

The peak at 18.50° is owing to $LiCoO_2$. From this data, the crystalline $LiCoO_2$ phase is clearly identified as rock-salt structured.³⁸ TG analysis of spent LIBs cathode material are carried to determine the pyrolysis temperature range as shown in Fig. 3a. a weight decrease of 5.25% at $344^\circ C$ is observed, which is corresponding to the decomposition of acid radical root and ammonium carbonate; From $480^\circ C$ to $690^\circ C$, the organic materials, such as resin membrane etc, are pyrolysed with a weight loss of 35.14%; the remaining remnants are owing the metal oxide anode after $800^\circ C$.

In order to further analyze metal elements in cathode material, XRF spectrometer are performed, it can be noted that the main metals exist including cobalt, manganese, nickel and copper, it's correspond to the content of 73.67 wt.%, 8.73 wt.%, 8.66 wt.% and 1.46 wt.%, respectively. The sum of the other elements is 7.48 wt.%. Compared to the main element, the sum of other elements is lower.

Fig. 1b shows the SEM images of the cathode material and it's obvious that the morphologies of LiCoO_2 is identified as irregular and agglomerated and nickel and manganese aggregate together, while combined with the characteristics of EDX (Fig. 1d), the main elements of the cathode material were C, Co, Ni and Mn, it can be inferred that LiCoO_2 are adhered to graphite layer, Fig. 1c shows the structure of the graphite materials which are not smooth layer.³⁹

3.2. Metal leaching with H_2SO_4 and H_2O_2

The present work respectively investigated the variation of leaching efficiency with H_2SO_4 concentration, temperature, reaction time, the dosage of H_2SO_4 and the amount of H_2O_2 . The $L_{16}(4^5)$ orthogonal experiment designed and the results are shown in the Table 3. The optimal experiment conditions are as follow: the reaction time 2.5 h, the reaction temperature 70 °C, H_2SO_4 of concentration 3.0 mol L^{-1} , the dosage of H_2SO_4 solid-liquid ratio 7 mL g^{-1} . Orthogonal test data above is not hard to find that the content of cobalt ion go up with the increasing of dosage of H_2O_2 . In order to further illustrate the relationship between the amount of Co^{2+} and H_2O_2 , five groups are chosen which operated with solid-liquid ratio ($\text{H}_2\text{O}_2/\text{cathode material}$) of 1.3, 1.4, 1.5, 1.6, 1.7 under the other optimal conditions. The test results shown in Fig. 4a. When $\text{H}_2\text{O}_2/\text{cathode material}$ is 1:1.6, the concentration of cobalt reach to maximum.

3.3. Effect of equilibrium pH on the concentration of metal ions in the leaching solution

In order to obtain cobalt with the optimal experiment, the relationship between the concentration of metal ions and the value of pH is investigated, and the results are shown in Fig. 5. Copper ion concentration changes indistinctively, manganese ion and nickel ion has a tendency to decrease, when the value of pH is increased from 3.00 to 3.70. When the value of pH is increased from 3.00 to 3.25, cobalt ion concentration falls sharply, but the cobalt ion concentration could remain constant within the pH value between 3.25 and 3.55. In order to maintain the larger cobalt ion concentration and lower the concentrations of manganese ion and nickel ion, pH value should be adjusted between 3.25 and 3.55.

3.4. Study on solvent extraction process

3.4.1 D2EHPA extraction of copper and manganese

When the pH of leaching liquid was adjusted to 3.50, the leaching liquid was filtered, then the extraction process was carried out. The results are shown in Fig.4b. From Fig.4b, Cobalt ions decreases gradually with the equilibrium pH increasing. It is obviously that manganese ion decrease when the the pH increase from 2.30 to 2.70, and keeping a low constant value when the pH value is up to 2.70, and the copper ion remains low constant value, so the copper and manganese ions could be removed mostly by D2EHPA extraction at the first extraction; In order to further remove copper and manganese ions, second extraction is required. First, the PH value of remain after the first extraction is adjusted, then copper and manganese ions are extracted by D2EHPA extraction. The results of second extraction are shown in Fig. 4c, the copper and manganese ions can separate effectively by D2EHPA extraction.

3.4.2 PC-88A extraction separation of cobalt and nickel

In order to improve the purity of cobalt ion, PC-88A extraction agent was applied to remove the nickel ions in the liquid phase. From Fig. 4d, it shows that cobalt ion drops rapidly in the liquid phase when PH value increase from 3.60 to 4.60. At the meantime, nickel ion also present a trend of decline in the liquid phase. It's suggested that nickel ion enrich in PC-88A extraction agent phase and the extraction ability of PC-88A is enhanced with the increase of pH. Therefore, the control pH value is lower to 4.25 make the concentration of cobalt ion to attain high value by the PC-88A extraction agent phase; at the same time, the concentration of nickel ion can maintain constant, so the cobalt ion and nickel ion could achieve the best separation effective. The best extraction recovery was 80.13% under the optimal extraction conditions.

3.5 Cobalt oxalate precipitation analysis

The SEM image (Fig. 6a) of cobalt oxalate is gained through D2EHPA extraction once and PC-88A once, the clear crystal structures are observed, but comparing with that through D2EHPA extraction twice and PC-88A once, which is shown in Fig. 6c, cobalt oxalate presents regular of acicular crystallization via twice extraction operation using D2EHPA. EDX spectra of the cobalt oxalate are shown in Fig. 6b and d, it clearly indicates that the relative content of manganese and copper ions in the

precipitation of cobalt oxalate are decreased after twice D2EHPA extraction.

Fig. 7 shows the XRD pattern and FTIR spectra of cobalt oxalate, the XRD pattern can be indexed as $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ crystals (PDF#25-0250) confirmed the well crystallized orthorhombic structure. The sharp peaks at $2\theta=19.07^\circ$, 22.84° , 30.33° , 30.05° are attributed to the reflections of (200), (002), (-402) and (021) planes of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.⁴⁰⁻⁴¹ From FTIR spectra, the strong peak at 3370 cm^{-1} is assigned to stretching vibration of the (O-H) group, which indicates the water of hydration. The peak at 1621 cm^{-1} and 1316 cm^{-1} are assigned to $\nu(\text{C-O})$ which is presence of oxalates with all four oxygen atoms.

The peak at 1360 cm^{-1} is due to the presence of carbonyl group.⁴² The peak at 825 cm^{-1} is assigned to $\delta(\text{O-C-O})$ band, while the band at 495 cm^{-1} is assigned to $\nu(\text{Co-O})$ and $\delta(\text{C-C-O})$,⁴³⁻⁴⁶ which indicated that the cobalt oxalate is gained. The main elements of the cobalt oxalate precipitation were dissolved in an acidic solution and analysed by ICP to determine the concentrations of cobalt. The results confirmed that the content of cobalt ion is accounted for 99.50 %. In addition, the deposition of the primary element are cobalt ($9.7630\text{ }\mu\text{g mL}^{-1}$), nickel ($0.0279\text{ }\mu\text{g mL}^{-1}$), manganese ($0.0069\text{ }\mu\text{g mL}^{-1}$), copper ($0.0050\text{ }\mu\text{g mL}^{-1}$) and iron ($0.0090\text{ }\mu\text{g mL}^{-1}$), the aluminum and cadmium were undetected by ICP.

3.6 Environmental and cost assessment

The increasing usage of lithium batteries will depend on the cost reduction and the recycling technique as well as the environmental conservation. As the LIBs industry where a major portion of the cobalt demand is met by the recycled cobalt from the spent LIBs, environmental technology will play very significant role in pricing the battery in future. Reliability and cost, environmental considerations must be taken into account. Considering the economic aspect, the attraction of recycling lithium-ion batteries depends on the metal market price as well as the electrode technologies used in lithium-ion batteries. Compared with the recovery of lithium, nickel and copper metal, recycling of cobalt is more meaningful, whereas cobalt recycling may be economically attractive. From an environmental and healthy view, lithium batteries can represent a significant hazard as these batteries contain hazardous materials.

Without proper disposal or recycling, lithium batteries may present potential threats to the environment and human health. Organic and inorganic compounds that can explode at high temperature or can pollute the environment. The battery is a potential fire hazard if not discharged completely. Furthermore, some of these inorganic or organic compounds are carcinogenic. So a proper recycling method is very important to environment.

This work focus on the complete route by the hydrometallurgy method to recycle cobalt from spent LIBs. After pre-treatment, reductive leaching, solvent extraction and selective precipitation, cobalt can be recovered. The leaching solution can be recovered and reused after extraction and separation of metal ions. By using diluted sulfuric acid washing extraction agent, the extraction agent can achieve the purpose of cobalt recycling. Theoretically, H₂O and O₂ are the only by-products in the leaching recovery process. Therefore, this green process may promise a closed-loop route for the sustainable recovery of metals from spent LIBs.

4. Conclusions

This work is focused on recycling cobalt from spent LIBs via green sustainable method, and the conclusions were obtained as follows:

1. The optimum leaching conditions are: contribution of factors affecting size ranked in the order: reaction time 2.5 h, H₂O₂ dosage 1.6 mL g⁻¹, H₂SO₄ concentration 3.0 mol L⁻¹, reaction temperature 70 °C, and the dosage of H₂SO₄ 7.0 mL g⁻¹.

2. The extraction of cobalt metal ion is based on the first step leaching experiment, using D2EHPA to extract copper and manganese and PC-88A which can be able to separate nickel and cobalt. D2EHPA saponification rate was 20%, the saponification PC-88A rate was 30%, the sulfonated kerosene accounted for the volume ratio of 70%, O/A ratio of 1:1. The first and second extraction pH of the aqueous solution is respective 2.70, 2.60 using D2EHPA. The pH of aqueous phase was adjusted to 4.25 using PC-88A.

3. Only in this way can the great purity of cobalt ion be get from spent LIBs cathode material. The purity of cobalt ion is up to 99.50% via determining the 0.5 mol L⁻¹ oxalic acid solution.

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Table 1
Solvent extraction techniques investigated by some previous references.

Extraction agents	Extraction conditions	Extraction of metal ions	References
Canex272	Stoichiometric ratio Cyanex 272/Co=4, pH 5-6	Co	[23]
D2EHPA	Stoichiometric ratio D2EHPA/Mn=2, pH 4	Mn	
Cyanex272	Cyanex 272 (monomeric basis) dissolved in diluent Exxsol D-80. Cyanex 272 sequence extracion: $Al^{3+} > Co^{2+} > Li^+$. The $pH_{1/2}$ values obtained are 3.0 for aluminium, 4.0 for cobalt and 6.5 for lithium.	Al, Co, Li	[24]
PC-88A	The extractant PC-88A was saponified by NaOH solution, sulfonated kerosene was used as the diluent and tri-n- butylphosphate was used as the phase modifier.	Co	[25]
Mextral5640H	Equilibrium pH of 2.06. 10 vol.% Mextral 5640H and A/O = 2:1	Cu	[26]
Mextral272P	Time-5 min, equilibrium pH of 5.50, A:O=2/1 and 30 vol.% Mextral 272P.	Co	

Table 2
Factors and levels of orthogonal experiment.

Factors	T(°C)	t(h)	[Acid](M)	[H ₂ O ₂](vol.%)	S:L(g mL ⁻¹)
Levels					
1	50	1.5	2.0	1:1.1	1:5
2	60	2.0	2.5	1:1.2	1:6
3	70	2.5	3.0	1:1.3	1:7
4	80	3.0	3.5	1:1.4	1:8

Table 3
Results of orthogonal experimental

Factors	t((h)	T(°C)	[Acid](M)	[H ₂ O ₂](vol.%)	S:L(g mL ⁻¹)	Co (µg mL ⁻¹)
The no.						
1	1.5	50	2.0	1:1.1	1:5	62.3040
2	1.5	60	2.5	1:1.2	1:6	65.4050
3	1.5	70	3.0	1:1.3	1:7	80.7720
4	1.5	80	3.5	1:1.4	1:8	79.0590
5	2.0	50	2.5	1:1.3	1:8	81.2700
6	2.0	60	2.0	1:1.4	1:7	77.6810
7	2.0	70	3.5	1:1.1	1:6	77.5780
8	2.0	80	3.0	1:1.2	1:5	79.8210
9	2.5	50	3.0	1:1.4	1:6	85.2770
10	2.5	60	3.5	1:1.3	1:5	84.6360
11	2.5	70	2.0	1:1.2	1:8	78.2030
12	2.5	80	2.5	1:1.1	1:7	78.0520
13	3.0	50	3.5	1:1.2	1:7	82.2800
14	3.0	60	3.0	1:1.1	1:8	78.4230
15	3.0	70	2.5	1:1.4	1:5	85.5380
16	3.0	80	2.0	1:1.3	1:6	79.5080
I	287.54	311.13	297.69	296.35	312.29	
II	316.35	306.14	310.26	305.70	307.76	
III	326.16	322.09	324.29	326.18	318.78	
IV	325.74	316.44	323.55	327.55	316.95	
i	71.88	77.78	74.42	74.08	78.07	
ii	79.08	76.53	77.56	76.42	76.94	
iii	81.54	80.52	81.07	81.54	79.69	
iv	81.43	79.11	80.88	81.88	79.23	
Extreme deviation	9.66	3.98	6.64	7.79	2.75	
Priority order	Time (h) > H ₂ O ₂ (vol.%) > Acid (M) > Temperature (°C) > S:L ratio (g mL ⁻¹)					
Optimal level	Time: 2.5 h; H ₂ O ₂ of dosage: 1.6 mL g ⁻¹ ; Acid of concentration: 3.0 mol L ⁻¹ ; Temperature: 70 °C; Solid-liquid ratio: 7.0 mL g ⁻¹					

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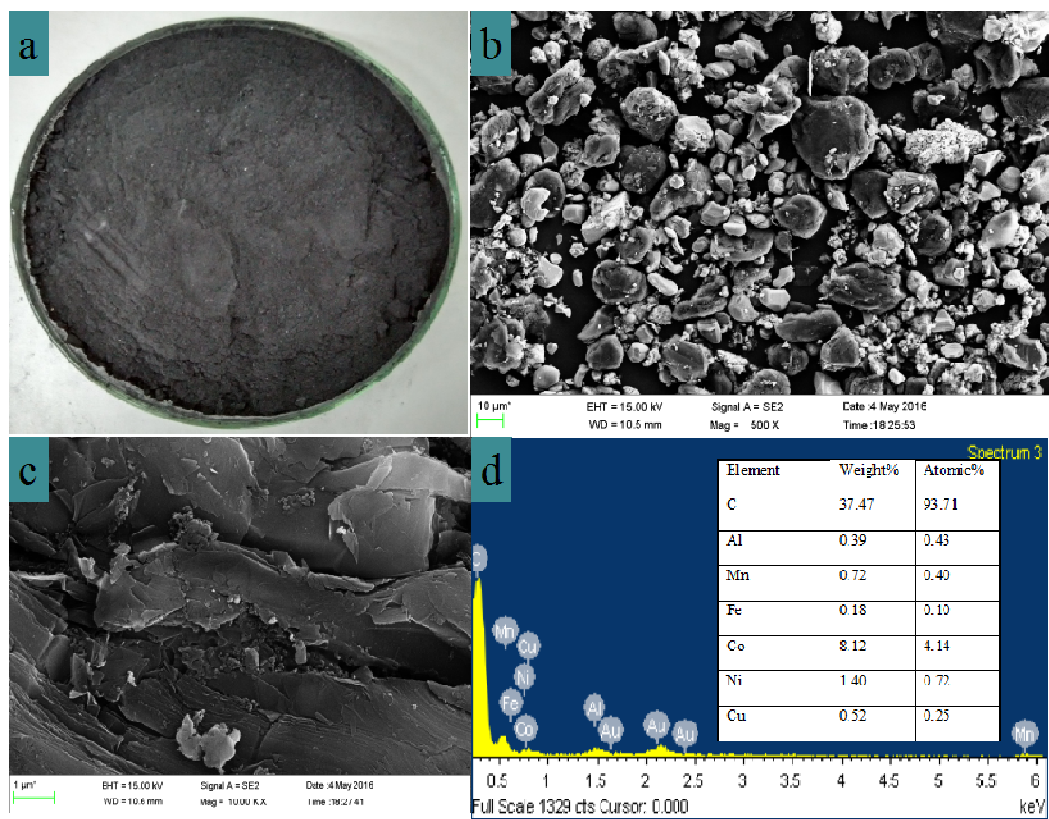


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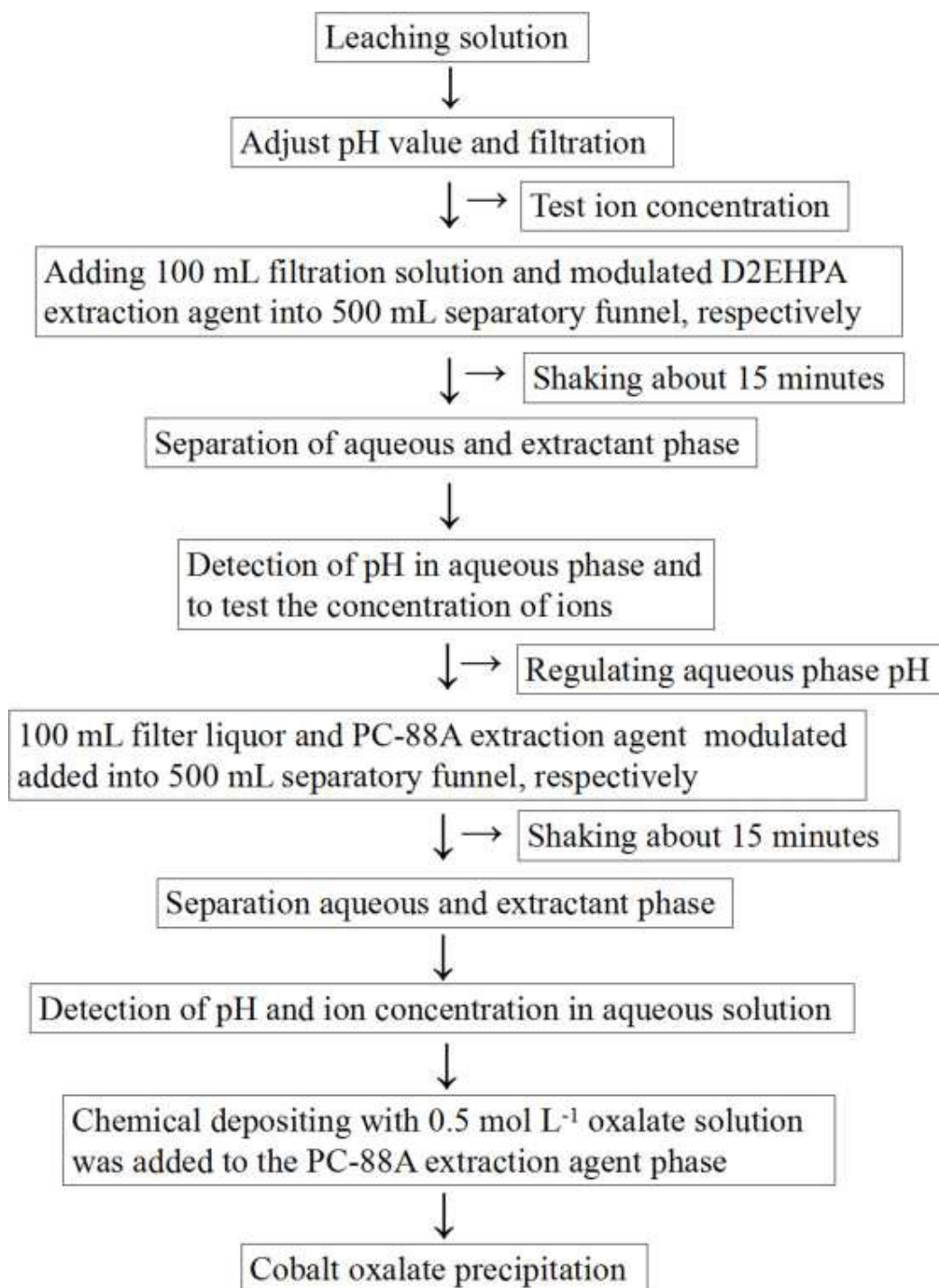


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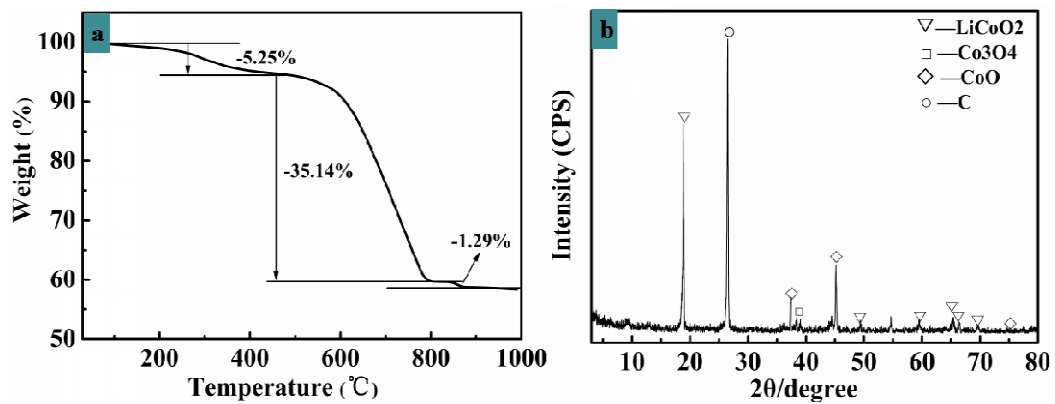


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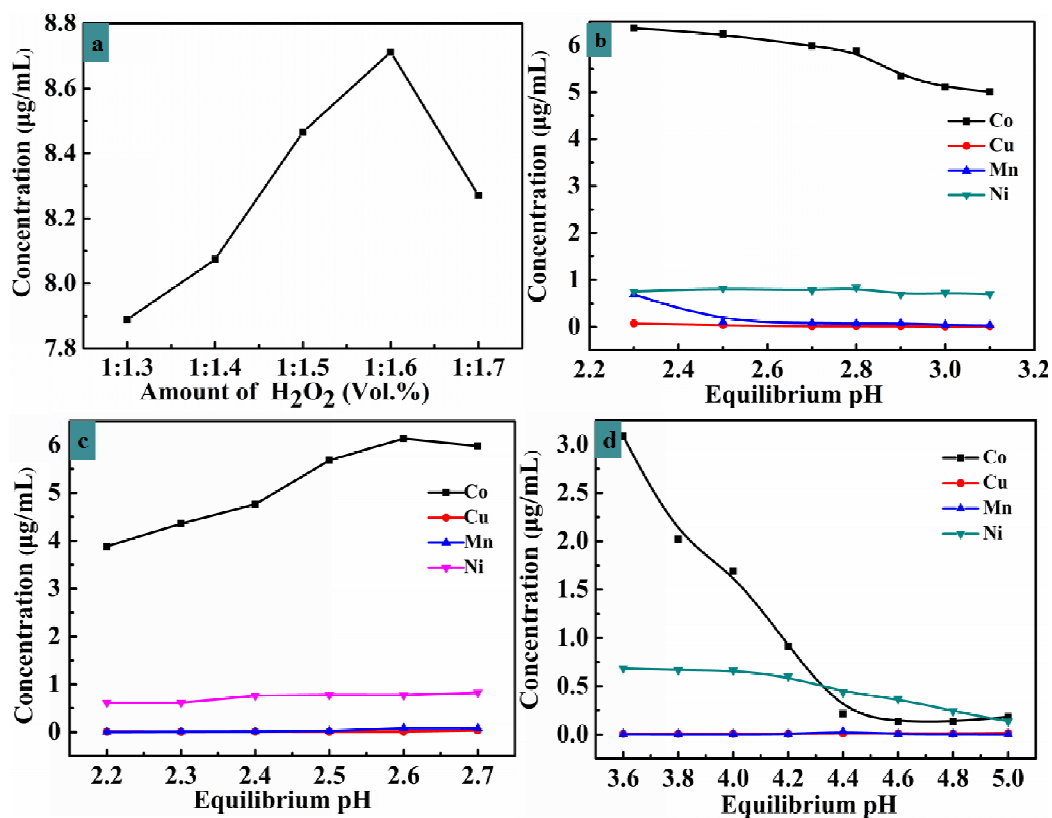


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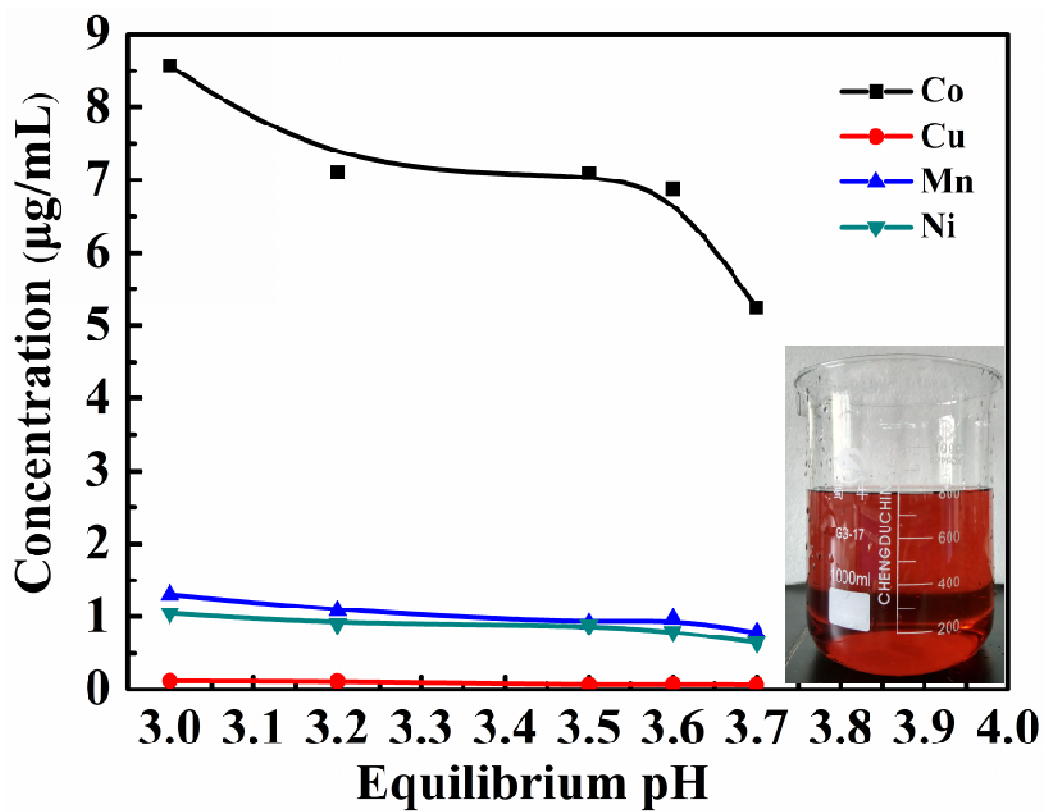


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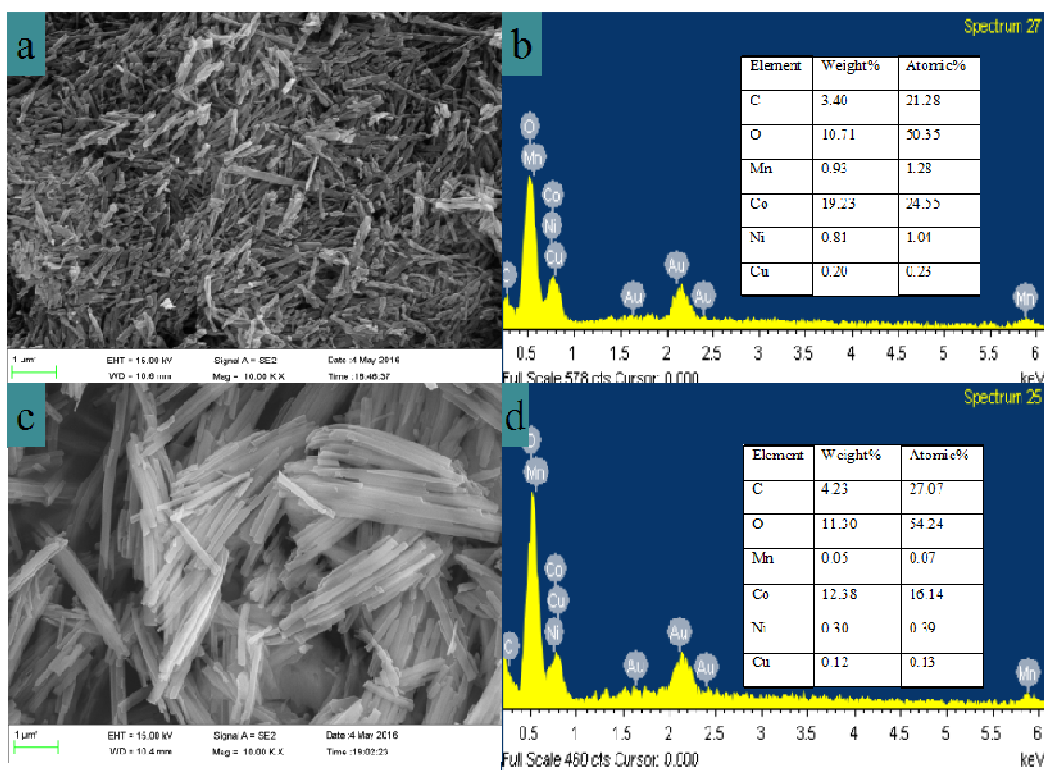


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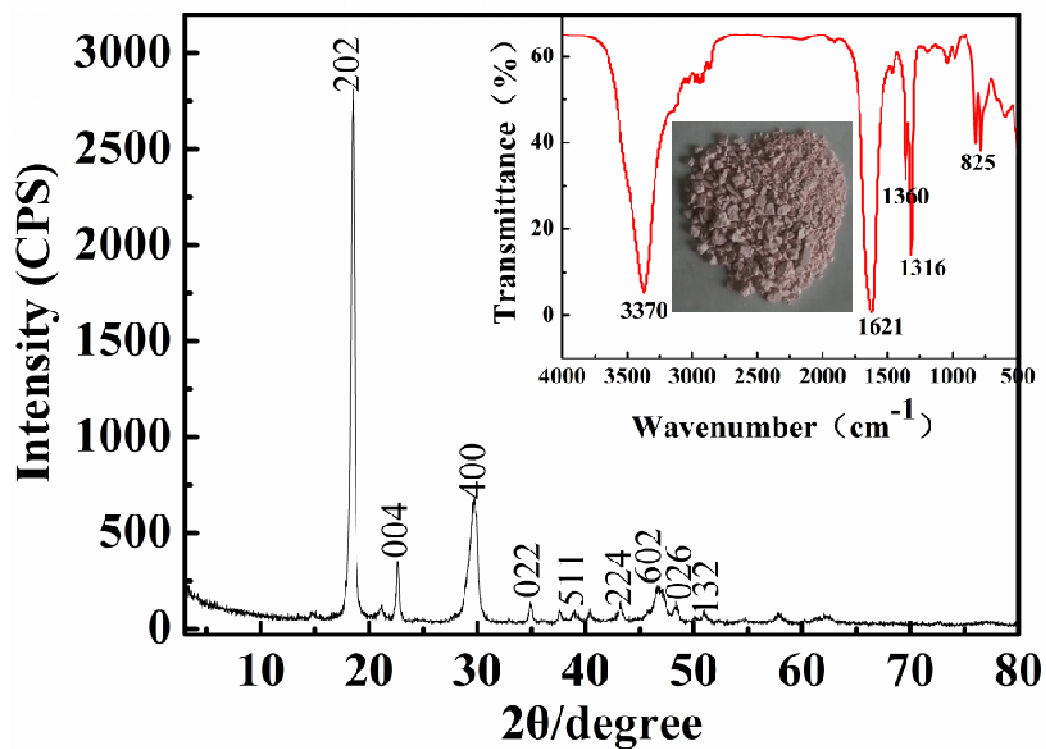


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