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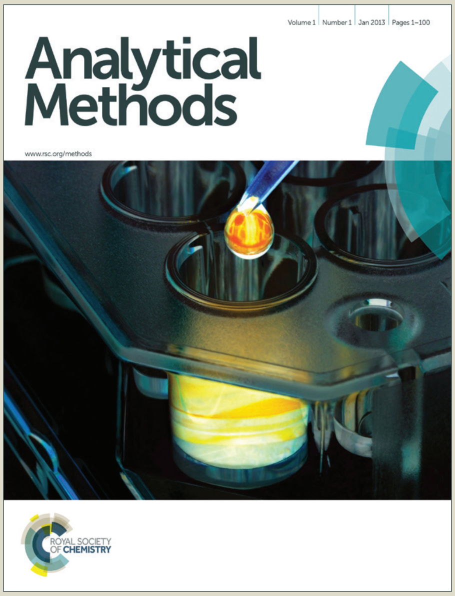

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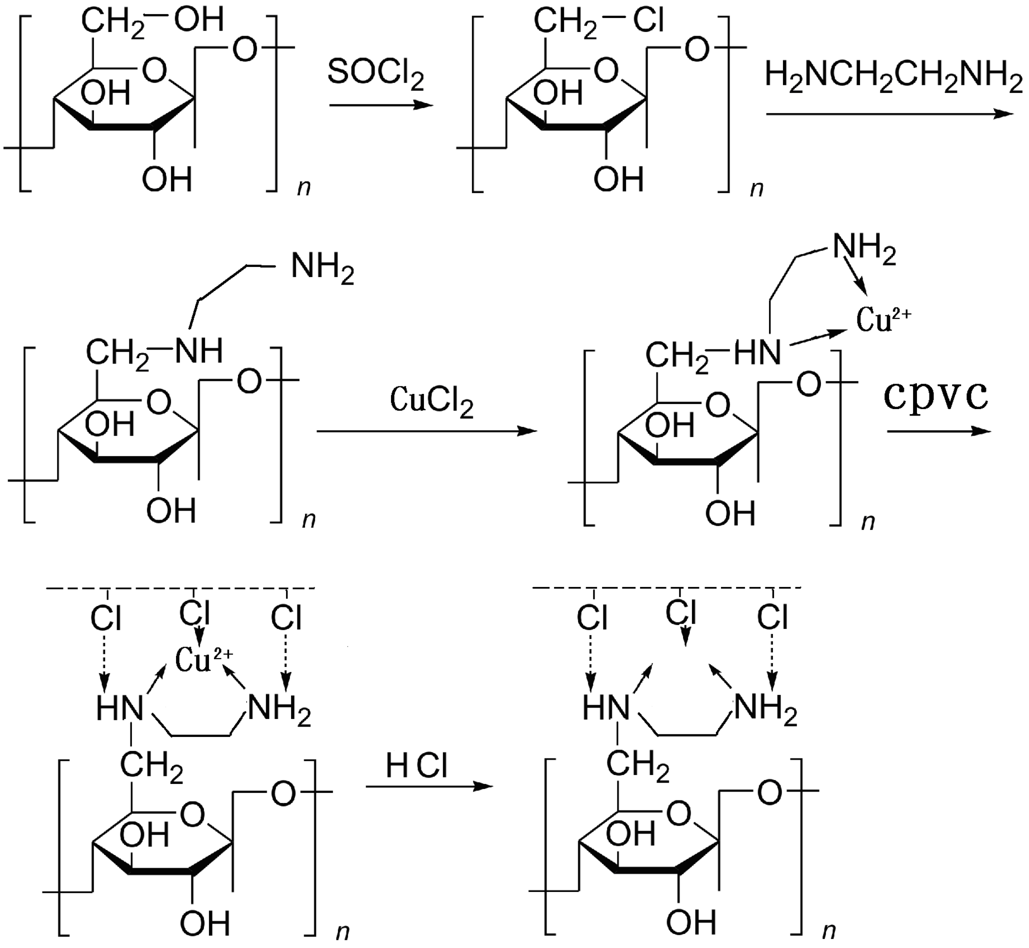
Preparation principle of a copper (II)-selective extraction disc （Cu^{2+}-SED） fabricated from Chlorinated Polyvinyl Chloride（CPVC） and Ethylenediamine-Functionalized Cellulose (Cell-EDA)



Fabrication and Application of a Copper (II)-Selective Extraction Disc Prepared from Chlorinated Polyvinyl Chloride and Ethylenediamine-Functionalized Cellulose

Lianchao Zhao,*[a,b] Hongtao Yan,[a] Caixia Yang,[b] Jiping Pan[b]

[a]College of Chemistry & Materials Science, Northwest University, Xian 710069, China

[b]Department of Environmental Engineering and Chemistry, Luoyang Institute of Science and Technology, Luoyang 471023，China

*e-mail: zlcly@lit.edu.cn Tel: 037965928271

Abstract Ethylenediamine-functionalized cellulose was prepared by the reaction of chlorinated cellulose and ethylenediamine. Next, the ethylenediamine-functionalized cellulose supported with copper (II) was prepared by the reaction of ethylenediamine-functionalized cellulose and $CuCl_2$. The powdered product was mixed with 1, 2-dichloroethane solution of chlorinated polyvinyl chloride, and then cast into a film and decoppered. Finally, the copper(II)-selective extraction disc was obtained. Using the copper(II)-selective extraction disc to the spectrophotometric determination of Cu^{2+} in solution, the linear range for Cu^{2+} analysis was 40–1100 μmol/L, and the detection limit was 38 μmol/L Cu^{2+}. In the repeatability test for analysis of 250 μmol/L $CuCl_2$ solution using the copper(II)-selective extraction disc, the relative standard deviation of seven determinations was less than 4.3%. The levels of Cu^{2+} in porcine liver and wastewater were determined using this method. The determination results had no significant difference as compared with those by atomic absorption spectroscopy. However, the new method is more economical.

Keywords Ethylenediamine-functionalized cellulose, chlorinated polyvinyl chloride, copper (II)-selective extraction disc, determination.

Introduction

Industrial wastewater often causes environmental pollution because of the presence of heavy metal ions. As heavy metal ions cannot be degraded in the environment and easily accumulate in organisms, even very low concentrations of heavy metal ions in wastewater can affect the survival of wildlife and endanger the health of human beings [1, 2]. Therefore, the detection of heavy metal ions in wastewater has long been a concern. The pretreatment method is commonly used for determining the levels of heavy metal ions with low concentrations in wastewater because of its high efficiency and economic applicability [1, 2]. The reaction between cellulose and other organic ligands is of particular interest in studies on the adsorption and enrichment of heavy metal ions [1,3,5–9] because of the characteristics of cellulose, such as good mechanical properties, thermal resistance, strong deformation resistance, and low cost. For example, Ethylenediamine-functionalized cellulose (Cell-EDA) was prepared by the reaction between cellulose and ethylenediamine after chlorination. Such functionalized cellulose has good adsorption capacity for Hg^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} [1, 3]. Thermodynamic analyses have proven that the adsorption of metal ions on Cell-EDA is an endothermic and spontaneous process [1]. Additionally, a catalyst supported with nanopalladium was prepared by using the reaction between Cell-EDA and $PdCl_2$ [4]. It is worth noting that the above adsorbents have good adsorbability but poor selectivity for metal ions. The levels of metal ions are determined and analyzed through subsequent separation. Improvements on the adsorption selectivity for metal ions could facilitate the determination and analysis of heavy metal ions in the solution.

In this study, Cell-EDA was prepared using degreased cotton as the raw material. The ethylenediamine-functionalized cellulose supported with copper (II) (Cell-EDA-Cu^{2+}) was obtained by the reaction between Cell-EDA and $CuCl_2$. Chlorinated polyvinyl chloride (CPVC) is a hydrophobic polymer with good optical stability, thermal resistance, and corrosion resistance [10, 11]. Chlorine atoms carrying partial negative charge are abundant in the molecule of CPVC. A 1, 2-dichloroethane solution of CPVC was used to treat the Cell-EDA-Cu^{2+}. After removing Cu^{2+}, the copper (II)-selective extraction disc (Cu^{2+}-SED) based on Cu^{2+} adsorption and enrichment by Cell-EDA was fabricated.

The interaction between the molecules of CPVC and Cell-EDA-Cu^{2+} was used to fabricate the Cu^{2+}-SED. When the Cell-EDA-Cu^{2+} was treated with 1, 2-dichloroethane solution of CPVC, the two types of molecules of CPVC and Cell-EDA-Cu^{2+} are connected closely because of the interaction between the molecules. The following interactions were involved: the interaction between chlorine atoms in the molecule of CPVC and the hydrogen atoms in the hydroxyl group of Cell-EDA; and the interaction between chlorine atoms and the hydrogen atoms in the ethylenediamine base and Cu^{2+}. When Cu^{2+} is removed, a “cavity” is retained. Since CPVC is insoluble in water and common organic solvents, the cavity can resist deformation caused by water and common organic solvents. With the amino groups and chlorine atoms that can react with Cu^{2+} by complexation, as well as the right size and shape of the cavity, the “memory” effect of the cavity to Cu^{2+} is produced. Therefore, the selectivity of Cu^{2+}-SED toward Cu^{2+} is produced

Since the cross-linking reaction is typically used in molecular/ionic imprinting technique, this method is more simple and practical than the methods based on molecular/ionic imprinting technique [12, 13]. The Cu^{2+}-SED was composed of filter paper and an adsorbent layer. Compared with the solid-phase extraction method [14–17], this method is more simple and convenient in operation. The preparation principle is shown in Figure 1.

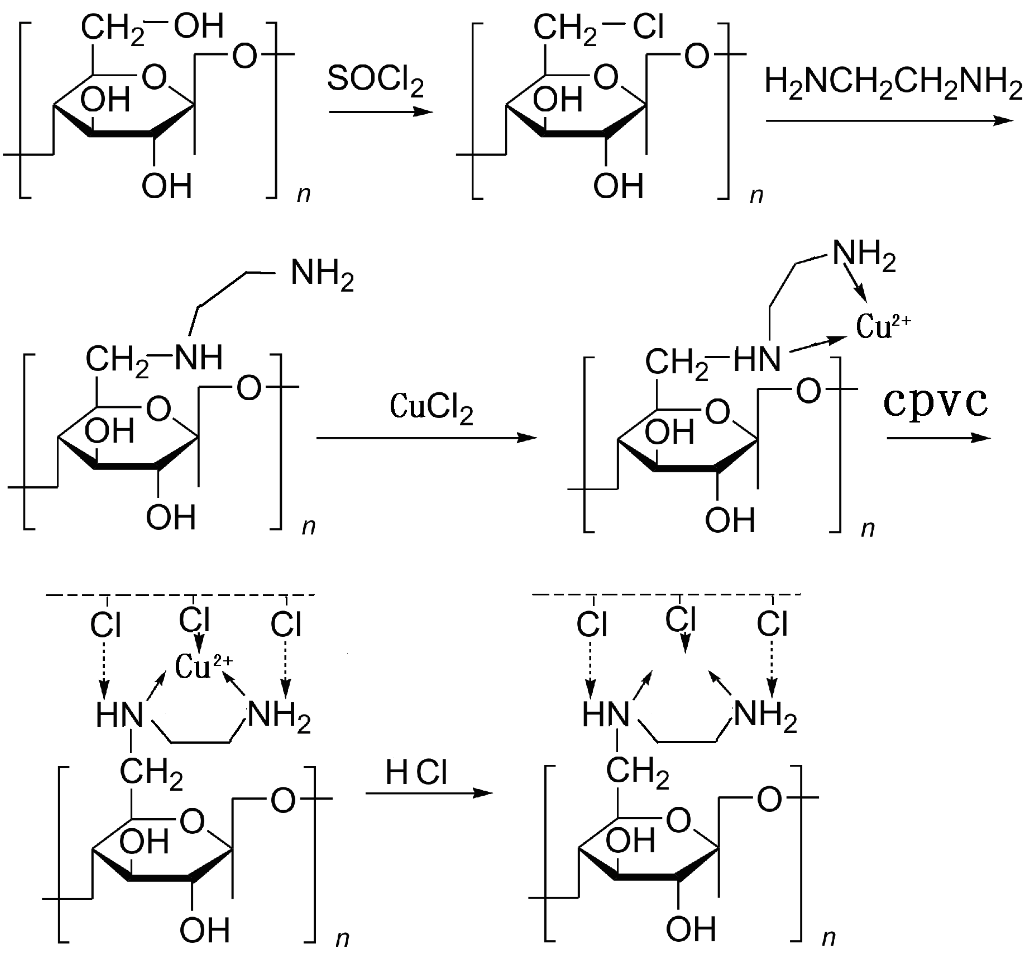


Fig. 1 Preparation principle of the Cu^{2+}-SED

1 Experiment

1.1 Instruments and Reagents

A 752(N) UV–vis spectrophotometer (Shanghai Jingke Electronics Co., Ltd., Shanghai, China) and a TAS-986 atomic absorption spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China) were used in this study.

Preparation of the standard solution of $CuCl_2$ was as follows: 0.1705 g copper chloride ($CuCl_2 \cdot 2H_2O$) was weighed accurately, and then dissolved in water to prepare 10.0 mmol/L standard solution of $CuCl_2$.

The $CuCl_2$ solution used in the experiment was prepared by dilution of this standard solution. Preparation of the detection reagent of Cu^{2+} was as follows: 0.1 g of sodium diethyldithiocarbamate was weighed and dissolved in 100 g water to prepare a 0.1 % (w/w) solution of sodium diethyldithiocarbamate. The CPVC resin was dissolved in 1, 2-dichloroethane to prepare solutions of CPVC with the weight percent concentrations of 4%, 6%, 8%, 10%, and 12%. The cellulose used in the experiment was from degreased cotton, and the filter paper was medium-speed qualitative filter paper (GB/T1914-2007, Hangzhou Whatman-Xinhua Filter Paper Co., Ltd.). All reagents used in the experiment were analytically pure, and the water was double-distilled water.

1.2 Preparation of Cu^{2+}-SED

1.2.1 Preparation of Cell-EDA

The Cell-EDA was synthesized according to the literature [3]. The bobbed degreased cotton (10 g) was weighed, and then combined with 200 mL dimethylformamide. The mixture was stirred and heated to 80 °C. $SOCl_2$ (35 mL) was added dropwise to the mixture, and the consequent reaction was allow to proceed at 90 °C for 2.5 h. The product obtained (chlorinated cellulose) was filtered, washed, and dried.

Chlorinated cellulose (10 g) was weighed, and then combined with 200 mL dimethylsulfoxide. The mixture was reacted with ethylenediamine at 100 °C for 12 h. The orange product obtained, Cell-EDA, was filtered, washed, and dried.

1.2.2 Preparation of Cell-EDA-Cu^{2+}

According to the literature [4], 0.4 g copper chloride ($CuCl_2 \cdot 2H_2O$) was added to 50 mL ethanol (95%), and the mixture was stirred. Afterward, 2.0 g Cell-EDA was added to the mixture for reaction at 60 °C for 4 h. The products were filtered, washed with water and ethanol, and then dried under an infrared lamp. The gray product, Cell-EDA-Cu^{2+}, was obtained.

1.2.3 Preparation of the Adsorbent Layer of the Cu^{2+}-SED

The homogeneous viscous liquid was obtained by intensive mixing of 0.04 g of Cell-EDA-Cu^{2+} and 0.3 mL of 1, 2-dichloroethane solution of CPVC. The viscous mixture was spread on filter paper (diameter: about 8 mm) using improvised tools. The filter paper coated with viscous liquid was cooled in a fuming cupboard to obtain the adsorbent layer (diameter: 5 mm, thickness: 0.7 mm). The surroundings of the adsorbent layer and the back of the filter paper were treated with 10% (w/w) 1, 2-dichloroethane solution of CPVC to avoid the adsorption of the solution and Cu^{2+} by the filter paper and to ensure that the Cu^{2+}-SED can float on the surface of the solution.

The adsorbent layer of the Cu^{2+}-SED was first wetted by 15% (v/v) ethanol solution, and then washed with distilled water. Next, the

Cu^{2+}-SED (adsorbent layer facing down) was placed on the surface of 0.5 mol/L hydrochloric acid solution. The solution was stirred to remove the Cu^{2+} from the adsorbent layer. The adsorbent layer from which the Cu^{2+} had been removed was washed with 10% (w/v) ammonia solution and distilled water, dried in air. Thereafter, the Cu^{2+}-SED was stored for later use.

1.3 Application of the Cu^{2+}-SED

The adsorbent layer of the Cu^{2+}-SED was first wetted with 15% (v/v) ethanol solution, and then washed with water. After that, the adsorbent layer was soaked in distilled water for 10 min.

The water adhering to the surface of the adsorbent layer was removed by filter paper. Afterward, the Cu^{2+}-SED was placed on the surface of the sample solution (adsorbent layer facing down). The Cu^{2+} in the solution was captured by the adsorbent layer of the Cu^{2+}-SED.

In order to reduce the amount of sample and reagents, the Cu^{2+}-SED was used to extract only a small portion of Cu^{2+} in the solution for the analysis of Cu^{2+}. The determination of Cu^{2+} was based on the facts that under the same experimental conditions, the amounts of the Cu^{2+} adsorbed by the adsorbent layer of the Cu^{2+}-SED is proportional to the concentration of Cu^{2+} in the sample solution.

The Cu^{2+} adsorbed by the adsorbent layer of the Cu^{2+}-SED was desorbed with 0.5 mol/L hydrochloric acid. Then detection reagent (0.3

mL) of Cu^{2+} was added to the hydrochloric acid solution and reacted with Cu^{2+} which had desorbed from the adsorbent layer of the Cu^{2+}-SED. The reaction product was extracted with 0.3 mL of trichloromethane. At 440 nm, the absorbance of the trichloromethane layer containing the reaction product was determined by spectrophotometry. The content of Cu^{2+} in the sample solution was obtained by a Cu^{2+} calibration curve.

The Cu^{2+}-SED could be recycled as it was still available after 90 cycles of testing. The adsorption capacity of the Cu^{2+}-SED used in this study for Cu^{2+} is 0.27 μmol (The adsorption capacity of the blank Cu^{2+}-SED is 0.11 μmol).

1.4 Adsorption characteristics

According to literature [12], Recovery (R) for Cu^{2+} was calculated according to the following equation:

$$R = \frac{n_e}{n_o} \times 100\%$$

where n_o and n_e are the number of moles of Cu^{2+}originally present in the sample and the number of moles of Cu^{2+} finally extracted in the adsorbent layer of the Cu^{2+}-SED, respectively. The distribution ratio (D) was also determined using n_2 and n_1.

$$D = \frac{n_2}{n_1}$$

where n_1 is the number of moles of Cu^{2+} in aqueous solution and n_2 is the number of moles of Cu^{2+} extracted in the adsorbent layer of the

Cu^{2+}-SED. Selectivity factor (S) is defined as:

$$S = \frac{D_{Cu}}{D_C}$$

where Dc is the distribution ratio of the ion which has been selected as reference.

1.5 Sample preparation

Sample 1: The porcine liver powder after drying (80 g) was weighed and then placed in an electric resistance furnace. The electric resistance furnace was kept at 500 °C for 24 h. The product of ashing was transferred to a beaker. A 10 mL of 6 mol/L hydrochloric acid was added to the ash, and the mixture was stirred and heated in a water bath. The products after heating were cooled and filtered. The filtrate was heated and concentrated to near dryness. Afterward, water was added to the filtrate, and the mixture was transferred into a 50 mL volumetric flask and diluted to the mark with water.

Sample 2: Wastewater (100 mL) taken from Ruzhou Coking Plant (China) was used as sample solution.

The digestion of two certified reference materials of YSS030-2006 zinc concentrate and GBW(E) 070107 lead ore (both provided by the Luoyang Aoxiang Chemicals and Instruments Co., Ltd., Luoyang, China) was operated as described in ref. [18]. 0.1000 g of YSS030-2006 zinc concentrate and GBW(E) 070107 lead ore were weighed and put into

PTFE（polytetrafluoroethylene）digestion vessels, respectively. After adding 5 mL mixture of HCI and $HClO_4$ (20 : 1 volume ratio), 3 mL of HNO_3 and 7 mL of HF, the vessel was capped and kept in the fuming hood for 10 h to allow thorough mixing of the sample and acids. The vessel was then heated at 210 ℃ and the mixture in the vessel was heated to near dryness. Next, 10 mL water and 3 mL mixture of HCI and HNO_3 (3:1 volume ratio) were added to the vessel, respectively. The mixture in the vessel was heated to a very small volume. The residue was dissolved with water and transferred into 50 mL volumetric flask. The resultant sample solutions were adjusted to pH 5 and diluted to the mark with water for analysis. The sample blank was prepared by the same procedure described above except that no analytes were added.

2 Results and Conclusion

2.1 Selection of CPVC Solution

In addition to Cu^{2+}, the Cell-EDA can also adsorb Hg^{2+} and Zn^{2+} [3]. Therefore, Hg^{2+} was firstly used as the reference to study the effect of the concentration of the 1, 2-dichloroethane solution of CPVC on the selectivity of the Cu^{2+}-SED. 250 μmol/L $CuCl_2$ solution and 250 μmol/L $HgCl_2$ solution were prepared. According to the procedure of preparing Cu^{2+}-SED described above, the Cell-EDA-Cu^{2+} was mixed with 1,2-dichloroethane solutions of CPVC with the weight percent concentration of 4 %, 6 %, 8 %, 10 %, and 12 %, respectively, and serial extraction discs made with Cell-EDA-Cu^{2+} were obtained. In the same way, the serial blank extraction discs made with Cell-EDA by mixing Cell-EDA with the same serial 1, 2-dichloroethane solution of CPVC were fabricated. Under the experimental conditions, all extraction discs were used to extract separately Cu^{2+} in 250 μmol/L $CuCl_2$ (0.3 mL) and Hg^{2+} in 250 μmol/L $HgCl_2$ (0.3 mL). According to the same experimental procedure described above, the Hg^{2+} was replaced by Zn^{2+} to investigate the effect of the concentration of the 1, 2-dichloroethane solution of CPVC on the selectivity of the Cu^{2+}-SED. As a comparison, the selectivity of the blank extraction discs was also investigated. The experimental results are shown in Figure 2.

As shown in Figure 2, when the concentration of the 1, 2-dichloroethane solution of CPVC exceeded 6%, S increased with the increase of the concentration of CPVC. This change can be explained as follows. With the increase in the concentration of CPVC, more cavities that can selectively adsorb Cu^{2+} form in the adsorbent layer of the Cu^{2+}-SED, and fewer amino-groups or chlorine atoms that can combine with metal ions by complexation are in the adsorbent layer of the Cu^{2+}-SED because of the interaction between the Cell-EDA-Cu^{2+} and CPVC. Additionally, with the increase in the concentration of CPVC, the sensitivity of the Cu^{2+}-SED in the detection of Cu^{2+} declined. In the present study, 8 % 1, 2-dichloroethane solution of CPVC was selected to prepare the Cu^{2+}-SED.

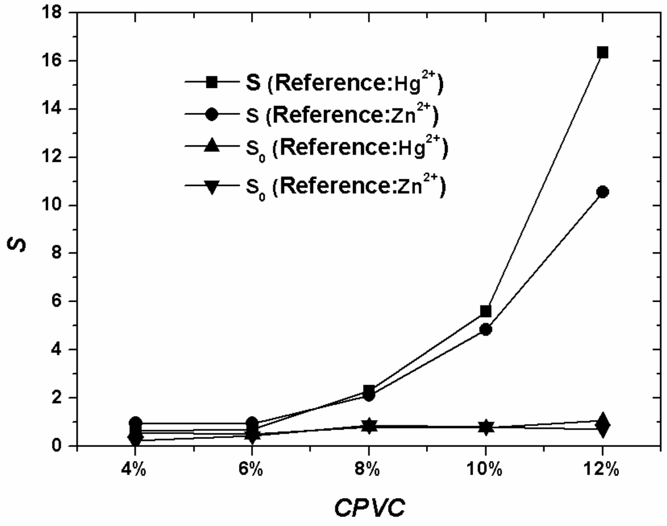


Fig. 2 Effect of the concentration of the 1, 2-dichloroethane solution of CPVC on the selectivity of the Cu^{2+}-SED (S and S_0 represents the selectivity of Cu^{2+}-SED and blank extraction discs, respectively)

2.2 Dosage of Sample and the Desorption of Cu^{2+}

250 μmol/L $CuCl_2$ solutions (0.1–0.5 mL) were used as the samples and analyzed with the Cu^{2+}-SED. The appropriate dosage of the sample was found to be 0.3 mL (Figure 3). The reagents used in desorption of Cu^{2+} from the Cu^{2+}-SED was 0.5 mol/L hydrochloric acid. The amount of hydrochloric acid and the time of desorption Cu^{2+} in the determination of Cu^{2+} was investigated and the experimental results are shown in Figure 3 and Figure 4, respectively. It can be seen from Figure 3 and Figure 4 that the appropriate amount of hydrochloric acid was 0.3 mL, and the appropriate time of desorption Cu^{2+} was 7 min. In these experiments, three replicate measurements were performed for each determination.

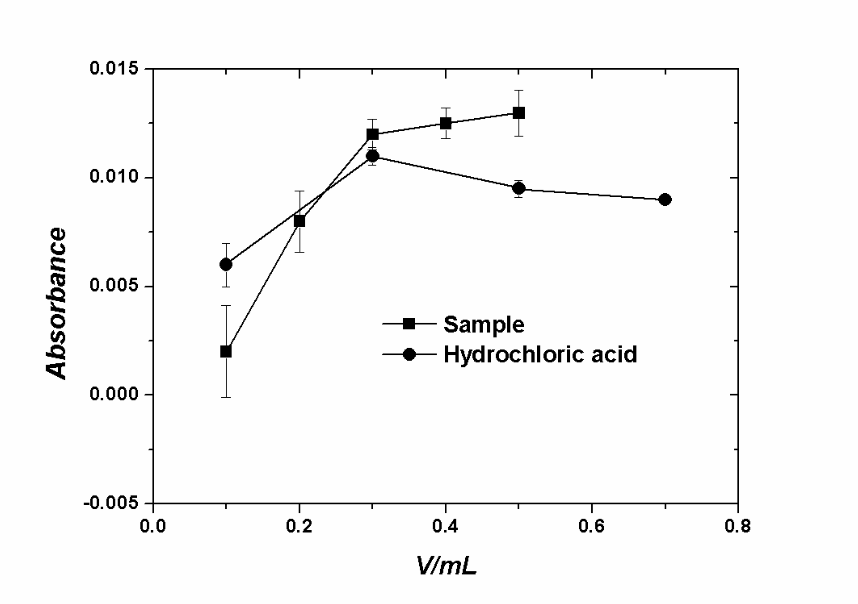


Fig. 3 Effect of sample amount and hydrochloric acid volume on the determination of Cu^{2+}

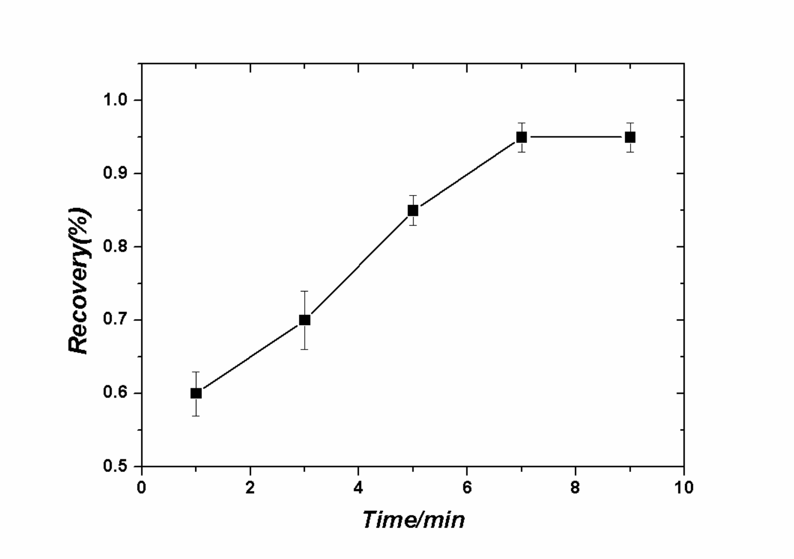


Fig. 4 Effect of desorption time on the determination of Cu^{2+}

2.3 Selection of Stirring Speed and Extraction Time

A 250 μmol/L $CuCl_2$ solution was used as the sample. The effects of stirring speed and extraction time on the determination of Cu^{2+} using the

Cu^{2+}-SED were studied in this experiment. Experimental results show that 100 rpm is the optimal stirring speed for the determination of the sample containing Cu^{2+} (Figure 5). The effect of extraction time on the determination of Cu^{2+} is shown in Figure 6. It can be seen from Figure 6, the extraction of Cu^{2+} by Cu^{2+}-SED is a slow process. The extraction equilibrium could not be obtained in less than 30 min; however, the recovery of Cu^{2+} stabilized at about 1.2 at 20 to 25 min. To improve the efficiency of determining Cu^{2+}, 20 min was selected as extraction time for the determination of Cu^{2+}.

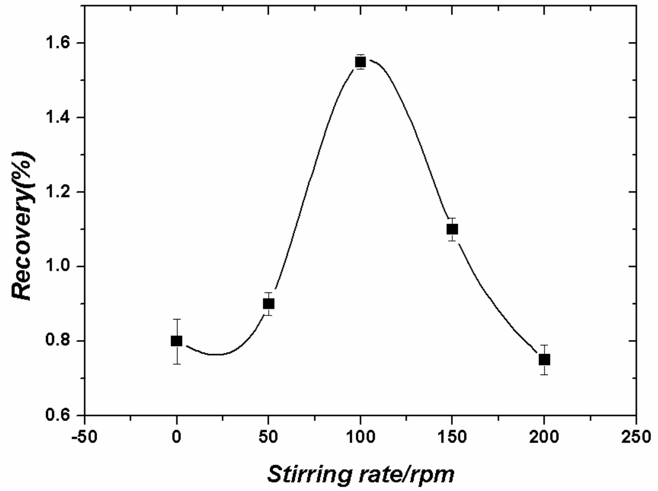


Fig. 5 Effect of stirring rate on determination of Cu^{2+}

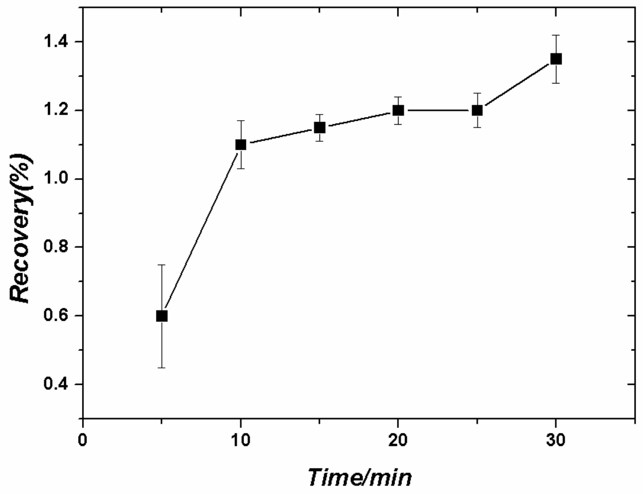


Fig. 6 Effect of extraction time on the determination of Cu^{2+}

2.4 Effect of Temperature

Under the selected conditions, 250 μmol/L $CuCl_2$ solution was prepared and used as the sample. The Cu^{2+}-SED was used for determining the solutions at solution temperatures of 15, 20, 25, 30, 35, and 40 °C by following the experimental procedures mentioned above. The experimental results are shown in Figure 7.

As shown in Figure 7, with the increase in the temperature, the recovery of Cu^{2+} increased within the range of 15–25 °C, and then showed little change within 25–35°C. Above 35°C, the recovery of Cu^{2+} increased rapidly with the increase in temperature. The experimental results are explained by the fact that increasing the temperature of sample solution results in different effects on the adsorption of Cu^{2+}. At first, the adsorption of Cu^{2+} on Cell-EDA was an endothermic and spontaneous process [1]; increasing the temperature of the sample solution favored the adsorption of Cu^{2+}. This was the reason why the recovery of Cu^{2+} increased with the increase in temperature of the sample solution in the initial phase. Next, with the increase in the temperature, the effects of thermal motion on the adsorption of Cu^{2+} increased. Within 25–35 °C, the change of the recovery of Cu^{2+} was dominated by the both positive and negative effects mentioned above. Above 35 °C, the intermolecular interaction of the Cell-EDA and CPVC was affected by thermal action caused by high temperature, which improved the adsorption capacity of the Cu^{2+}-SED. However, its selectivity of adsorption was lowered. In this study, the experiment temperature was set at 25 °C.

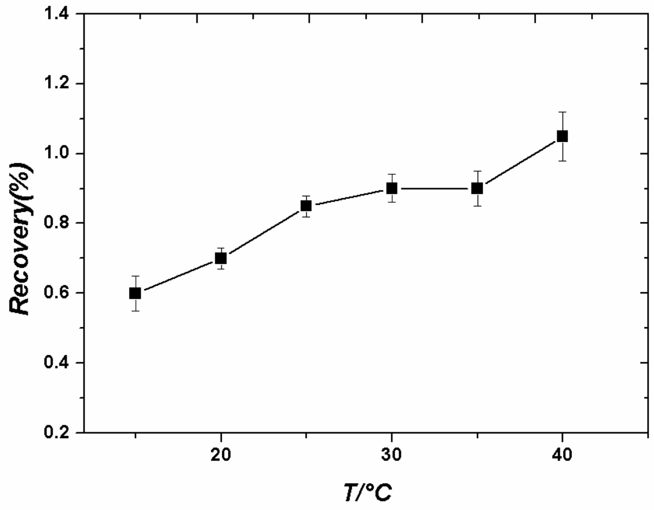


Fig. 7 Effect of temperature on the determination of Cu^{2+}

2.5 Effect of pH on the Determination of Cu^{2+}

The effect of pH was studied in this experiment. A series of 250 μmol/L $CuCl_2$ solutions with pH values of 1, 3, 5, 7, and 9 were prepared. Under the selected conditions, the solutions were analyzed according to the experimental procedures using the Cu^{2+}-SED. Experimental results show that the recovery of Cu^{2+} increased at pH 1 to 5. The maximum value is about pH 5, and then it decline rapidly. With the reduction of solution pH at pH 1–5, there were more amino-groups and chlorine atoms that combined with H^+ in the adsorbent layer of the Cu^{2+}-SED. This impaired the adsorption of Cu^{2+} on Cu^{2+}-SED and resulted in the reduction of the recovery of Cu^{2+}. In the range of pH > 5, since the hydrolysis reaction of Cu^{2+}, the concentration of Cu^{2+} decreased with the increase in solution pH. Therefore, the recovery of Cu^{2+} decreased with the increase in solution pH. Clearly, the optimal pH of the solution for determining Cu^{2+} with the Cu^{2+}-SED is 5.

2.6 Repeatability, Linear Range, and Detection Limit

A 250 μmol/L $CuCl_2$ solution was analyzed by using the Cu^{2+}-SED. Under the experimental conditions, the average value of seven determinations was 0.018; the relative standard derivation was less than 4.3%.

Under the selected experimental conditions, the series of $CuCl_2$ standard solutions (30–2000 μmol/L, 0.3 mL) was analyzed using the Cu^{2+}-SED. The pH of the solution was adjusted to 5 with 1 mol/L hydrochloric acid. The detection results confirm that the linear range of the concentration of solution containing Cu^{2+} analyzed by spectrophotometry with the Cu^{2+}-SED is 40–1100 μmol/L, and the detection limit is 38 μmol/L.

2.7 Interference Experiment

The experimental results show that when the $CuCl_2$ solution was analyzed using the Cu^{2+}-SED, there were no significant interferences from solutions with concentrations 500 times (Na^+, K^+ and NH_4^+), 200 times (Hg^{2+}, Cr^{3+}, Cd^{2+}, Zn^{2+}, and Pb^{2+}), 100 times (Fe^{3+}), 10 times (Co^{2+}), and 2 times (Ni^{2+}) of 250 μmol/L ($CuCl_2$ solution) within the error range of ±5%.

2.8 Comparison of different methods for determining Cu^{2+}

The comparison of this study with other extraction and molecular imprinted technique for determination Cu^{2+} is shown in Table 1. Compared with the Ref. [12, 16], this study method is faster (compared with Ref. [12]) and a small volume of eluent and sample is required to achieve quantitative results in determining Cu^{2+}. Besides, the linear range of this study is larger than Ref. [12, 16], and the fabrication of the adsorbent used in this study is easier than that in Ref. [12, 16].

Table 1 Comparison of this study method with other methods in determining Cu^{2+}

Contents	Ref.[12]	Ref.[16]	This study
Forming recognition sites	Cross-linking reaction	Bonding reaction	Intermolecular action
Elution volume	10 mL	2 mL	0.3 mL
LOD	0.14 $\mu g\cdot L^{-1}$	0.24 $\mu g\cdot L^{-1}$	$2.4\times10^{3}\mu g\cdot L^{-1}$
Elution time	8 h	–	7 min
Sample volume	25 mL	300 mL	0.3 mL
Adsorption time	3 h	15 min	20 min
linear range	50–200 $\mu g\cdot L^{-1}$	0.8580 $\mu g\cdot L^{-1}$	2.5×10^{3}–$7.0\times10^{4}\mu g\cdot L^{-1}$

2.9 Sample Detection

This study method has been applied to the determination of Cu^{2+}in certified reference materials (YSS030-2006, zinc concentrate, and GBW (E) 070107, lead ore). The results (0.75 ± 0.01(%) and 0.87 ± 0.01(%)) obtained were good agreement compare to the certified values (0.77±0.01 (%) and 0.85±0.02 (%)) using a t-test at 95% confidence limits. To assess the applicability of this study method to real samples with different matrices, the sample was analyzed by the method in the present study and by atomic absorption spectroscopy [19]. Meanwhile, the spike recovery of the sample was determined. The results are shown in Table 2. The results in Table 2 show that there was no significant difference in the content of Cu^{2+} in the sample determined by the method in the present study as compared with that determined by atomic absorption spectrometry.

Table 2 Results of the detection of Cu^{2+} in the samples (*n* = 6)

Samples	This study method		Atomic absorption spectroscopy[19]	
	Determined*	Spiked with 30 μmol/L $CuCl_2$ (Recovery, %)	Determined*	Spiked with 30 μmol /L $CuCl_2$ (Recovery, %)
Sample1	203.13±7.72	31.13±1.09 (103)	205.3±10.7	31.75±1.43 (106)
Sample2	250.00±11.75	31.25±1.41 (104)	257.1±15.2	28.72±1.41 (96)

*Average of six measurements, mean ± S.D.

3 Conclusions

The Cell-EDA easily adsorbs and binds Cu^{2+} ion. Moreover, the CPVC resin is insoluble in water or common organic solvents, and has a strong intermolecular interaction with the Cell-EDA. On the basis of these characteristics, the Cu^{2+}-SED with selectivity toward Cu^{2+} was prepared. The present study provides an economical and practical method for the analysis of Cu^{2+} in water solutions. Meanwhile, it paves a new way for the development of molecular/ionic imprinting techniques. Additionally, the method in the present study is an improvement on the conventional solid-phase extraction. The method features easy construction of the device, convenient operation, and low detection cost.

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