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A new chelating resin from waste printed circuit board powder

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Abstract. An aminated resin was prepared by using the waste printed circuit board(WPCB) powder, with brominated epoxy resin as the polymer matrix material, pretreated with acid and alkali, then modified using diethylenetriamine. A novel chelating resin containing a dithiocarbamate(DTC) group was synthesized with the reaction by the aminated resin, carbon disulfide and Sodium hydroxide. It was characterized by FTIR and ¹³C NMR. The adsorption effects of the modified materials on heavy metal ions were investigated, and the results showed that DTC-WPCB have well adsorption performance on Ag⁺.

1.Introduction

Printed circuit board (PCB) is the basis of electronic industry, which was widely used in a variety of electronic products. With the increasing number of waste electronic equipment in recent years, the number of WPCB has risen sharply^[1]. In addition, enhanced industrial activity during recent decades has led to the discharge of unprecedented volumes of wastewater, which is a serious cause of environmental degradation, the problem of water pollution caused by heavy metals is also becoming seriously^[2]. The removal of heavy metal ions in wastewater were mainly chemical precipitation^[3], membrane technology^[4], ion-exchange method^[5], electrochemical treatment^[6] and chemical adsorption^[7]. Among them, the chemical adsorption using chelate resins is the most commonly used method of treating heavy metals in waste water. There are various chelat resins reported in literatures^[8-14], but most of them have higher cost of polymer matrix used in the synthesis. WPCB is a mixture of approximately 30% metal and 70% nonmetal. The nonmetallic materials in WPCB is mainly brominated epoxy resin, which is feasible polymer matrix of synthesizing chelat resins. Bromine atoms are more active in brominated epoxy resins and are a prerequisite for material modification^[15,16]. At present, the research about WPCB recycling is mainly concentrate on recovery of high-valued metals or precious metals, but nonmetallic materials recycling is less pronounced^[17]. The recycling technology of nonmetallic solid wastes in WPCB is mainly including pyrolysis, incineration, landfill and physical recovery methods to prepare composite materials^[18-20]. The above



methods are not fully consistent with the concept of environmental safety, follow the economic cycle model, so a new economic and environmentally friendly recycling technology is in need.

In this paper, brominated epoxy resin in WPCB was used as a modified raw material to synthesize a dithiocarbamic(DTC)-WPCB chelate material and was used to adsorb heavy metals in industrial wastewater. The structure of the chelate material was characterized by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance(NMR). The adsorption properties of metal ions on the chelate material were also studied.

2. Experimental

2.1 Materials and instruments

WPCB was obtained from a factory in China. Diethylenetriamine(ETA), potassium carbonate, cuprous iodide, dimethyl sulfoxide(DMSO), carbon disulfide, and ethanol were also used. Ag^+ solution was prepared by silver nitrate as the simulation wastewater. The pH value was altered by HNO_3 and NaOH solution. All the chemical reagents were analytically pure and were used without any further purification.

The UV-visible absorbance spectra of the samples were measured using WFX-110A spectrophotometer (Beijing Ruili Analytical Instrument Co, Beijing, China). Fourier Transform Infrared (FTIR) spectroscopy was recorded by AVATER 370 instrument (Nicolet, USA). PH measurements were carried out with PHBJ-260 pH meter (Shanghai, china). The ^{13}C NMR data was obtained from the AVANCE III HD 500MHz (Bruker Biospin, Switzerland).

2.2 Modification of WPCB

Waste printed circuit board solid wastes are mainly brominated epoxy resin and glass fiber, which brominated epoxy resin was considered as the polymer matrix for the modification in this experiment (Figure 1).

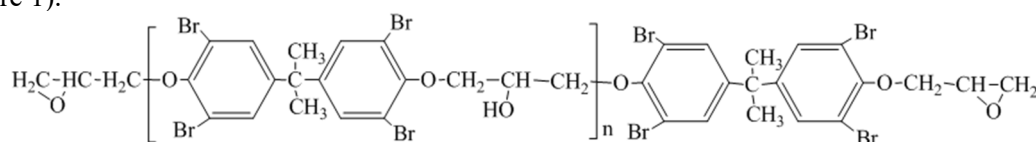
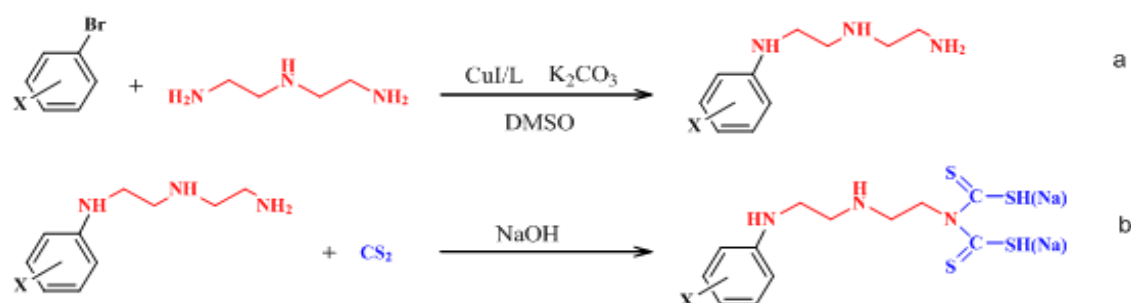


Figure 1. Structure of brominated epoxy resin.

The collected solid waste was pulverized with water by pulverizer, take the wet powder 200 g washed several times. And then followed by acid pickling, alkali washing, and water washing, to the filtrate was neutral. Filtering, drying the powder at $100\text{ }^{\circ}\text{C}$. The DTC-WPCB chelate material was synthesized by two steps (Scheme 1).

The pretreated brominated epoxy resin(30 g) was added to a four-necked flask and swollen with 300 ml of dimethylsulfoxide at room temperature for 2 h. CuI (3.81 g) was added into the solution as catalyst, L-proline(4.60 g) was added as ligand. After stirring for 1.5 h at $40\text{ }^{\circ}\text{C}$, diethylenetriamine(50 ml) was added to conduct amination. Then, K_2CO_3 (2.78 g, 1 mol) dissolved in distilled water(20 ml) was transferred to a constant pressure dropping funnel and added slowly to the flask. Put them at $90\text{ }^{\circ}\text{C}$ for 8 h with reflux and continuous stirring. After the reaction nearly complete, the mixture was washed successively with water, ethanol, and dried at $50\text{ }^{\circ}\text{C}$ after filtered to obtain a modified amination resin(Scheme.1.a).

The modified amination resin(30 g) was added to a three-necked flask and swollen with 8% sodium hydroxide solution(40 ml) at $30\text{ }^{\circ}\text{C}$ for 2 h. 4 ml of carbon disulfide was added and reacted at $30\text{ }^{\circ}\text{C}$ for 8 hours. Then the reaction was continued at $50\text{ }^{\circ}\text{C}$ for 8 hours with reflux and continuous stirring. After the reaction complete, the mixture was cooled, filtered, washed with deionized water to neutral, washed with ethanol and dried at $50\text{ }^{\circ}\text{C}$ to obtain a chelating material containing dithiocarbamate group(Scheme.1.b), its structure was confirmed by FT-IR and ^{13}C NMR spectroscopy.



Scheme 1 (a)Synthetic route of modified amination resin.(b)Synthetic route of DTC -WPCB chelating material.

3.Results and discussion

3.1 Characterization of DTC-WPCB

The FTIR spectra of WPCB and DTC-WPCB were presented in Figure 2. The broad band in the WPCBs spectrum at $3600\text{ cm}^{-1} \sim 3100\text{ cm}^{-1}$ with a maximum at 3428.52 cm^{-1} , was assigned to stretching vibrations of -OH. The peak at 3428 cm^{-1} in the spectrum of WPCB was shifted to 3373 cm^{-1} in that of modified DTC-WPCB, the peak area narrowed down, and it was assigned to the stretching vibration peak of -NH which superimposed with the -OH peak. The new peak at 1604 cm^{-1} in spectrum of DTC-WPCB is a characteristic absorption peak of C=N. Compared to WPCB, the two peaks at 1509 cm^{-1} and 1449 cm^{-1} in the DTC-WPCB spectrum were ascribed to the compound vibration of -C(=S) and -NH-. In the spectrum of WPCB, the new peak at 1234 cm^{-1} was attributed to the C-N stretching vibration absorption peak. The peaks at 1037 cm^{-1} and 829 cm^{-1} are the C=S stretching vibration peak and the C-S stretching vibration absorption peak, respectively.

The existence of these characteristic peaks confirmed that dithiocarbamate groups were successfully chelated with brominated epoxy resins in WPCB.

By comparing the spectra of raw material and modified chelate material, it was clear that changes generated in the structure of the materials. Raw material was complex ingredient, which contained high proportion of insoluble inorganic components, but low levels of brominated epoxy resin. Therefore, we mainly analyzed the nuclear magnetic spectrum of the modified chelate material.

The ¹³C NMR (400MHz, DMSO-d₆) data of the synthesized DTC-WPCB were: δ : 189.06(d, 2C, C=S), 94.89(s, C, -Ar-Br), 38.72(q, 4C, N-CH₂-CH₂-N-CH₂-CH₂-N).

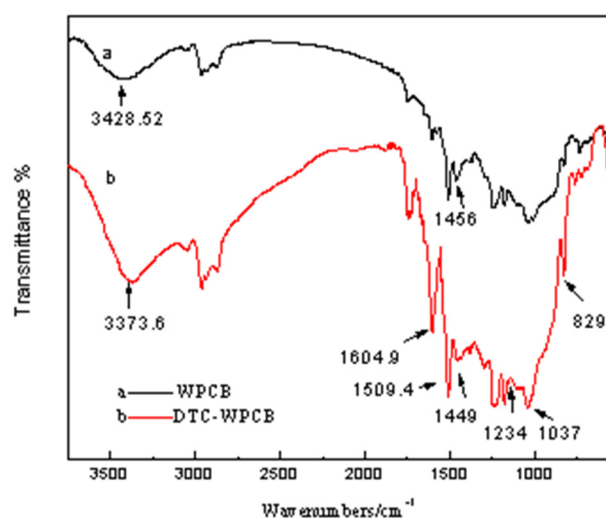


Figure 2. FTIR spectra of WPCB and modified chelate material.

3.2 The adsorption of heavy metals in waste water by DTC-WPCB

The adsorption of Ag^+ was carried out by the raw materials, the modified aminated materials and the final dithiocarbamate chelate materials to further verify the structure changes of the modified chelate material.

20 mL of Ag^+ solution ($C = 9.8635 \text{ mg/L}$, $\text{pH} = 7$) were added to each of 0.4 g of raw material, modified aminated material and modified chelating material, respectively, and adsorbed at 25°C for 3 h. The test results are shown in Table 1.

The results indicated that raw material for Ag^+ was substantially non-adsorbed because there was no chelating adsorption site. The modified aminated material could adsorb part of Ag^+ , because the grafted diethylenetriamine has a certain chelating ability. The dithiocarbamate chelate material functionalized by carbon disulfide and sodium hydroxide showed a good adsorption effect on Ag^+ , and the adsorption rate reached 100%, because the Dithiocarbamic acid groups has good chelate ability to Ag^+ . Thus, it is possible to further verify the successful process of amination and the functionalization of carbon disulfide and sodium hydroxide.

Table 1 Adsorption data of Ag^+ before and after modification

Adsorption material	residue after adsorption $C/\text{mg}\cdot\text{L}^{-1}$	Adsorption rate/%
Raw materials	9.5003	3.68
Modified aminated materials	4.7010	52.34
Modified chelating material	0	100.00

4. Conclusions

Through the recovery and modification of the brominated epoxy resin in the solid waste of the printed circuit board, we have prepared a new chelate resin capable of adsorbing on Ag^+ , and realized the purpose of recycling the resources. The structure of the modified chelate was characterized by IR and ^{13}C NMR. The datas showed that the structure of the modified chelate has a dithiocarbamate group, which confirmed the success of the reaction. The adsorption tests of the material before and after the

modification on Ag^+ were performed. The data showed that the raw material has no adsorption capacity, the aminated material has a certain adsorption capacity, and the chelate material obtained by the functionalization of the dithiocarbamate has a good adsorption performance for Ag^+ .

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