# Synthesis and Characterization of Thiosemicarbazide Fiber

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**Abstract**. A novel sulfur ion exchange fiber - thiosemicarbazide chelating ion exchange fiber (TSCIEF) was prepared by nucleophilic substitution reaction of chloramethylated polypropylene graft styrene (CPP-g-St) fiber and thiosemicarbazide, using anhydrous ethanol as swelling agent. The structure of TSCIEF was characterized through IR, TG, DTG and SEM testing. The adsorption capacity of TSCIEF on Au (III) were evaluated. The results showed that the adsorption capacity of TSCIEF on Au (III) was 142 $mg \cdot g^{-1}$. What's more, the TSCIEF has an excellent selective adsorption on Au (III) in mixed solution. Infrared spectra indicated that chloridion on the benzene ring was substituted by thiosemicarbazide group. TG and DTG confirmed that TSCIEF was more stable than PP-g-St under the same temperature. The optimum adsorption pH value is 2.

## Introduction

As a new kind of high polymer adsorbing material, chelating ion exchange fiber has lots of advantages. It is diverse, largely adsorptive and selective. This kind of fiber can change physical and chemical structure of material according to different needs. It is one of the hottest research fields with great application future and high research value. And chelating ion exchange fiber with ligating atom (such as N and S), especially thiourea fiber, has excellent adsorption properties and selective adsorption[1]. Xue Ailian[2] reacted chloromethylation of polystyrene and glucosinolates semicarbazide, and got polystyrene glucosinolates semicarbazide chelating resin. It has a good adsorption capacity for Ag (Ⅰ), Cu (II), Pb (II) and Cr (III). However, studies on chelating ion exchange fiber reacted by thiosemicarbazide is relatively less[3-4]. From the point of molecular structure, thiosemicarbazide has higher reactivity and better adsorption property. So, thiosemicarbazide chelating ion exchange fiber has better adsorption property and selectivity[5].

In this study, TSCIEF was prepared by CPP-g-St fiber. This work is based on the research of chelating ion exchange fiber by our research group[6-10]. The effects of the reaction conditions were investigated to optimum the synthesis process.

## Experiments

**Reagents.** HCl, NaOH, $CH_3COOH$ (Beijing Chemical Co., Ltd.), thiosemicarbazide (Shanghai Hushi Industry), CPP-g-St (Guilin Hanzheng Co., Ltd.). All of the chemicals and reagents used were analytical grade and were used without further purification.

 

**Instrument.** PHS-3C acidity (Shanghai Precision & Scientific Instrument Co., Ltd.), SHA-B plate thermostatic oscillator (Guohua Co., Ltd.), XS105DU electronic analytical balance (Mettler -Toledo Instrument Co., Ltd.), the characteristic functional groups of the fiber were identified by infrared spectrophotometer (Bruker EQUINOX55). Surface morphology of fabric samples was assessed using scanning electron microscopy (SEM HITACHI S4300F) and all fabric samples were dried using vacuum drying method and spray gold processed before the testing. The concentration of Au (III) in aqueous solution is measured by ICP-OES directly does not dilution.

**Thiosemicarbazide alkylation experiment.** CPP-g-St was fully swelled in anhydrous ethanol and thiosemicarbazide completely dissolved in the aqueous solution. After that the CPP-g-St fiber and thiosemicarbazide solution with a fix ratio were added to a three round bottom flask, and the mixture was suspended by a stirrer. The reaction was carried out at a fixed temperature for a period of time. When the reaction was finished, pour out the reaction liquid, the result fiber was washed to neutral by deionized water, then washed by anhydrous ethanol two or three times. The TSCIEF was got after dried in vacuum drying oven to constant weight.

**The determination of fiber adsorption capacity.** The TSCIEF prepared under different conditions which weighed accurately was put into Erlenmeyer flask with 25.00 mL $HAuCl_4$ solution inside. The flask was oscillated in fix temperature and 120 rpm rotation speed for 24 h. The concentration of Au (III) in aqueous solution is measured by ICP-OES directly. The adsorption capacity of TSCIEF for Au (III) was calculated according to the formula following:

$$q = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where $c_0$ and $c_e$ are the concentration of initial and equilibrium Au (III) ion solution concentration, respectively; $V$ is the volume of cyanide aqueous solution (mL); $m$ is the mass of TSCIEF (g).

## Results and Discussion

**Reaction mechanism.** A nucleophilic substitution was happened by the chloralkane on the CPP-g-St and thiosemicarbazide. Thiosemicarbazide attack the chlorine methyl of benzene nucleus as nucleophile. The following is the reaction equation:

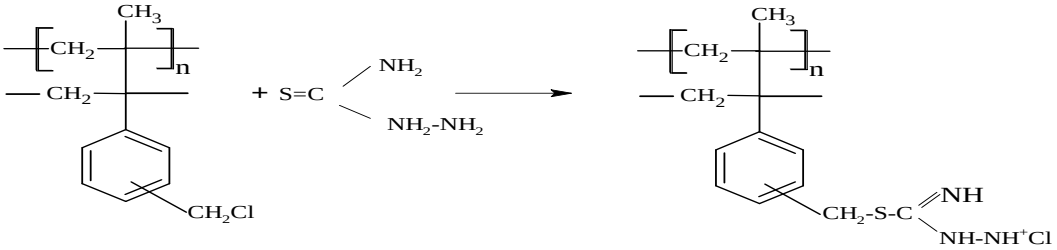


**Fig.1** The reaction mechanism

**IR analysis result.** Infrared spectrum of Material fiber (a), TSCIEF before and after Au (III) adsorption (b, c) were given in Fig.2.

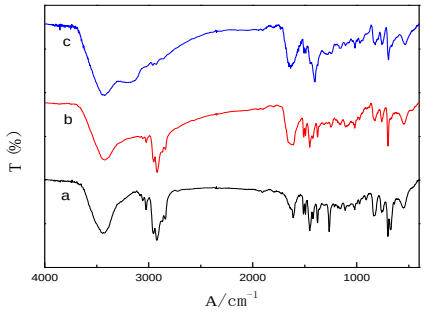


**Fig.2** Infrared spectrum of fiber

According to the curve (b), stretching vibration peak of C=S emerged at 1080 $cm^{-1}$, the absorption peak intensity enhanced around 1622 $cm^{-1}$, as the -$NH_2$ groups exist, the C-Cl bond absorption peak at 829 $cm^{-1}$ and 669$cm^{-1}$ are greatly weakened and even disappeared. All of these explain the emergency of nucleophilic substitution reaction. Curve (c) shows the infrared spectrum TSCIEF after adsorption Au (III), absorption peak of -$NH_2$ around 3430 $cm^{-1}$ are weakened which can explain -$NH_2$ participated in the adsorption process. And peak near the 3000 $cm^{-1}$ and 1362 $cm^{-1}$ almost disappeared, along with emergence of new adsorption peak around 1392 $cm^{-1}$ shows that the TSCIEF adsorption of Au (III) is a complex chemical adsorption process.

**SEM analysis result.** SEM images of Material fiber (a), TSCIEF before and after Au (III) adsorption (b, c)were given in Fig.3.

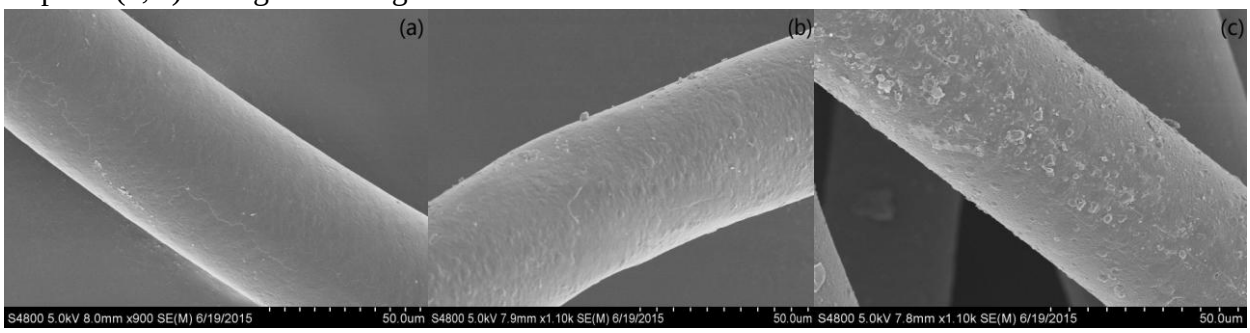


**Fig.3** SEM images of fiber

As observed from image, raw material fiber is cylindrical with smooth surface, uneven phenomenon was appeared in TSCIEF surface, and surface uneven phenomenon become more obvious, and there are many granular material after Au (III) adsorption.

**TG and DTG analysis result.** Fig.4 and Fig.5 gave TG and DTG of raw material fiber and TSCIEF.

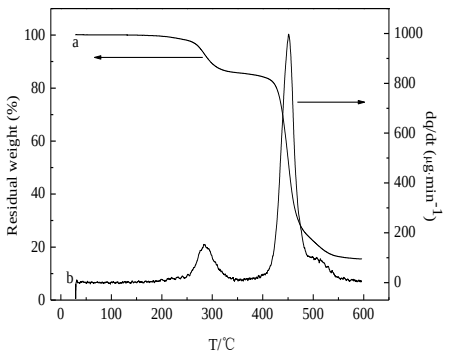


**Fig.4** TG and DTG curve of raw material

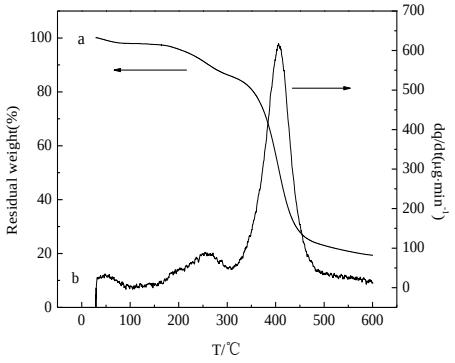


**Fig.5** TG and DTG curve of TSCIEF

When the temperature reached to 250 ℃, the weightlessness of raw fiber is less than 2%, and 14% when 350 ℃. This is the acyl chloride falling off process. TSCIEF lose weight from 200 ℃, the first phase of weightlessness by about 16%, this phase should be the loss of HCl groups. Another 8% were lose when 350 ℃, this phase should be the loss of S=N groups. TSCIEF has good thermal stability performance as weightlessness is less than 4% within 200 ℃.

**Effect of pH value on adsorption capacity.**

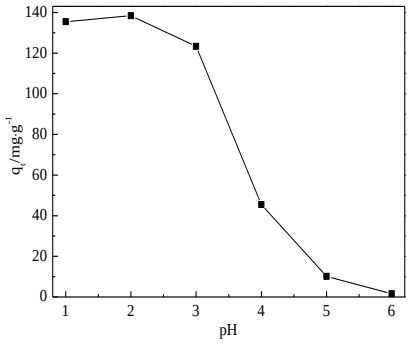


**Fig.6** The effect of different pH value

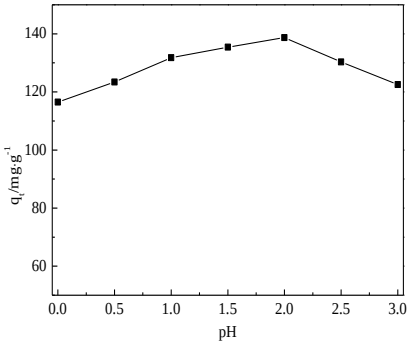


**Fig.7** The effect of strong acid

Fig.6 and Fig.7 shows the curve of pH value effect, and strong acid condition was considered in Figure 6. The data shows that the optimum pH value is around 2. TSCIEF can work well in strong acid condition.

**Selective adsorption.** Two same quality of TSCIEF affecting the same concentration of Au (III) and Cu (II) solution respectively. Detect the concentration of the ions in solution after adsorption equilibrium. Table 1 shows the results.

**Table 1** The comparison of TSCIEF selective adsorption to metal ions from water

| Fiber | Au (III)（mg·g$^{-1}$） | Cu (II)（mg·g$^{-1}$） |
|---|---|---|
| TSCIEF | 130.54 | 0.56 |

The data shows that the TSCIEF has a good adsorption capacity on Au (III), but for Cu (II), there almost has no adsorption. So TSCIEF has good selective adsorption performance of Cu (II) and Au (III) mixture solution.

## Summary

(1) IR, TG, DTG and SEM testing proving the new fiber's synthesized successfully in this experience. And TSCIEF has good thermal stability performance as weightlessness is less than 4% within 200 ℃;

(2) Adsorption experiments shows that the TSCIEF has an good adsorption capacity on Au (III), and the saturated adsorption capacity can be achieved 130.54 mg·g$^{-1}$. What's more, TSCIEF can work well in strong acid condition and it has a good adsorption capacity on Au (III) from the Cu (II) and Au (III) mixture solution.

## References

[1] S.Wang. The synthesis and adsorption of Polyester base of thiourea resin [D]. Changsha: Central South University, 2008.

[2] A.L.Xue, S.C.Shen. Synthesis and adsorption on heavy metal ions of polystyrene glucosinolates semicarbazide chelating resin [J]. Chemical Industry Times, 2014, 28(12): 1-4.

[3] C.P.Liu, L.Sun, J.B.Lv. Ion Exchange and Adsorption [J]. 2005, 21(4): 335-342.

[4] B.Gong, Y.Wan, Anal. Bioanal. Chem [J]. 2002, 372(4): 597-600.

[5] X.Jiang, C.H.Ni, C.P.Zhu. The synthesis and adsorption of thiosemicarbazide-formaldehyde chelating resin [J]. Ion Exchange and Adsorption, 2008, 24(2): 118-123.

[6] M.Y.Li, Q.X.Zeng, C.G.Feng. The structure and performance of strong alkaline ion exchange fiber [J]. Materials Science and Technology, 2006, 14(1): 32-35.
[7] Q.Deng, Q.X.Zeng, C.G.Feng. Polypropylene base strongly basic anion exchange fiber structure characterization and performance study [J]. Journal of Materials Science and Engineering, 2006, 24(5): 642-645.
[8] X.L.Sun. Preparation and application of chelate fiber [D]. Beijing: Beijing Institute of Technology, 2009.
[9] M.Y.Li, H.G.Zhao, Q.X.Zeng. The synthesis and adsorption of amino phosphonic acid chelate fiber [J]. Journal of Functional Materials, 2012, 43(5): 550-554.
[10] Y.R.Sun. The preparation and application chelating fibers based polypropylene [D]. Beijing: Beijing Institute of Technology, 2013.