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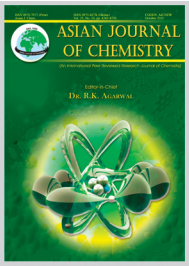

# Synthesis of New Type Cross-linked Chitosan Porous Resin and the Absorption of Cd(II) and Ni(II)

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Chitosan is a versatile material, its derivatives has a wide range of applications. Chitosan resin absorption metal ions, becomes a research hotpot in recent years. A new chelating resin using chitosan as a base material was synthesized. Functional moiety of tetraethylenepentamine (TEPA) chemically bonded to the amino group of cross-linked chitosan (CCTS) through the arm of chloromethyloxirane, ethylene glycol diglycidyl ether (EGDE) as the cross linker. The risen was holed by PEG-2000 to get porous-CCTS-TEPA. The amine resin showed a higher affinity towards the uptake of Cd(II) and Ni(II) from neutral solution, where an uptake value of 123.54 mg/g and 262.50 mg/g, porous-CCTS-TEPA uptake value of 220.86 mg/g and 315.0 mg/g respectively at pH 7 and room temperature.

**Key Words: Cross-linked chitosan tetraethylenepentamine, Cd(II), Ni(II), Absorption porous.**

## INTRODUCTION

With the development of industry, the amount of production and use of cadimium and nickel are continuously raise. Their compounds are widely used in galvanization, alloy manufacture, batteries, *etc.*[1,2]. Heavy metal ions in natural water can bring harmful effect to human health, as well as to animals and plants in aquatic environment[3]. In human body, cadmium and nickel could harm many organs[4,5] and was involved into carcinogen role by international agency for research on cancer and national toxicology program[6].

Usual treatments for extraction of metal ions from effluents consist of flotation, solvent extraction, precipitation, ion-exchange and electrochemical separation, these methods sometimes suffer from problems such as excessive time requirements, high costs and production of highly toxic sludges[7]. Chitosan was modified by compound which have amido and hydroxyl group to adsorb heavy metal ions is a hotspot in recent years[8-10]. Cross-linked chitosan (CCTS) was chemically functionalized with serine diacetic acid moiety through the extension arm of chloromethyloxirane, then the resin was modified with tetraethylenepentamine, PEG-2000 as the porogen, study the absoption Cd(II) and Ni(II) capacity of tetraethylenepentamine modified cross-linked chitosan (CCTS-TEPA).

## EXPERIMENTAL

Chitosan (Shang Hai Lanji Corporation), benzaldehyde (AR, Tian Jin Ke mi Ou Chemical Corporation), ethylene glycol diglycidyl ether (EGDE) (AR, Shang Hai Ru Fa Corporation), epichlorohydrin (AR, Sinopharm Chemical Regent Co. Ltd.), PEG-2000 (AR, Sinopharm Chemical Regent Co. Ltd), standard solution of cadmium(II) (Sinopharm Chemical Regent Co. Ltd.), standard solution of nickel(II) (Sinopharm chemical regent Co. Ltd.), $CdCl_2.5H_2O$ (AR, Sinopharm Chemical Regent Co. Ltd), $NiCl_2.H_{20}$ (AR, Sinopharm Chemical Regent Co. Ltd), tetraethylenepentamine (AR, Sinopharm Chemical Regent Co. Ltd) were obtained.

**Instrumentations:** Nicolet-670 (NEXUS USA), atomic absorption spectrometer (East and West analytical, AA-7003). SEM (KYKY-EM3900M).

**Synthesis of CCTS-TEPA resin:** Chitosan was reacted with benzaldehyde (80 g) in order to protect the amino group. The protected-chitosan was then filtered by using filter paper and washed with ethanol to remove the remaining benzaldehyde, followed by washing with water. The cross-link structure was made by refluxing the protected chitosan with EGDE (30 g). The product was then filtered and washed with ethanol and water, respectively. The Schiff base was cleaved to recover amino group by stirring the product in 0.5 M hydrochloric acid (500 mL). The cross-linked chitosan was then filtered and washed three times with water. In the second step, the cross-linked chitosan was modified by introducing serine moiety through chloromethyloxirane extension arm. The cross-linked chitosan (5 g) was reacted with chloromethyloxirane (10 g) in order to attach the extension arm. The product was

then filtered using filter paper and washed each three times with ethanol and water to remove the remaining chloromethyloxirane[3]. The cross-linked chitosan, which has chloromethyloxirane as an extension arm, was then reacted with the tetraethylenepentamine. The synthesis scheme of CCTS-TEPA is shown in Fig. 1.

Put 100 mL atolein, a little of span-80 and PEG-2000 into flask, stirred for 0.5 h, put CCTS-TEPA into the flask, stirred for 1 h. The product was then filtered using filter paper and washed each three times with ethanol and water to remove the remaining atolein, to get porous-CCTS-TEPA.

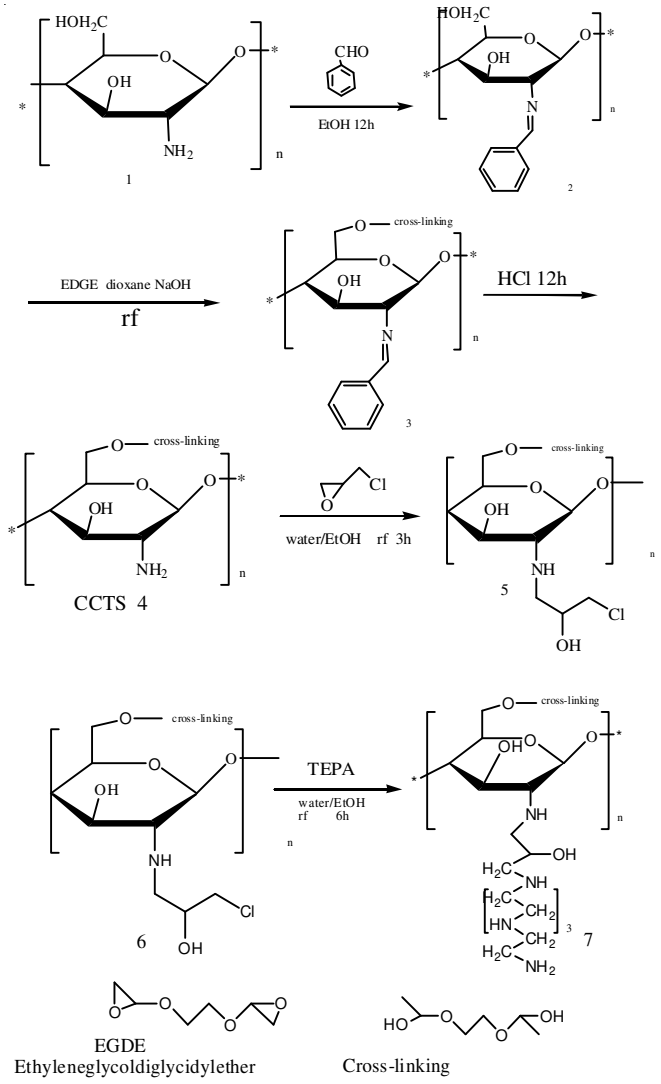


Fig. 1. Synthesis of CCTS-TEPA

**Ions absorption experiment:** Put 0.2 g CCTS-TEPA in the solution of $Cd^{2+}$ and stirred for 5 h, the remaining powder was filtered using filter paper. And then repeated the experiment with the solution of $Ni^{2+}$ with porous-CCTS-TEPA.

## RESULTS AND DISCUSSION

**Characteristics of CCTS-TEPA resin and CCTS-TEPA-Cd:** The IR spectrum of CCTS-TEPA resin and CCTS-TEPA-Cd resin (which has been obtained by absorbed $Cd^{2+}$) were shown in Fig. 2. The overlapped absorption peak removed to low wavenumber from 3300 $cm^{-1}$. The transmogrification absorption peak shifted to 1650 $cm^{-1}$ from 1600 $cm^{-1}$, the phenomenon indicated formation of the Cd-N bond. The electron doublet moved to the $Cd^{2+}$. The absorption peak was not evident changed in 1000 $cm^{-1}$, it show that the absorption process did't breach the glucose ring. The IR spectrum of CCTS-TEPA-Ni is similar with CCTS-TEPA-Cd. The transmogrification absorption peak observed at 1612 $cm^{-1}$ from 1600 $cm^{-1}$, the phenomenon indicated the formation of Ni-N bond.

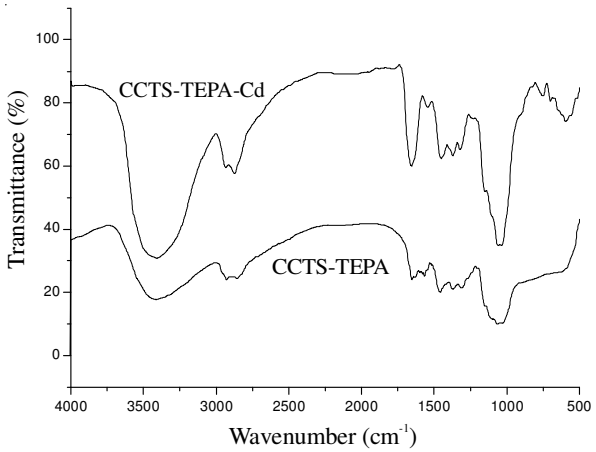


Fig. 2. FT-IR spectra of CCTS-TEPA and CCTS-TEPA-Cd

### Factor affecting the absorption prosess

**pH Affecting the absorption prosess:** The absorption ability of the resin (CCTS-TEPA and porous-CCTS-TEPA) was mensurated at room temperature. Put 0.2 g resin into the $Cd^{2+}$ solution. The pH of the solutions were 2, 3, 4, 5, 6, 7. It is calculate that CCTS-TEPA could absorb 123.54 mg/g $Cd^{2+}$ at room temperature at pH = 7,while the porous-CCTS-TEPA could absorb 220.86 mg/g $Cd^{2+}$ in the same condition. It CCTS-TEPA absorbs 262.50 mg/g $Ni^{2+}$ at room temperature and pH = 7, while the porous-CCTS-TEPA could absorb 315.00 mg/g $Ni^{2+}$ in the same condition. The absorption ability of the resin was get the maximum in pH = 7. In acidity condition, the electron doublet of N atom could found coordinate bond with $H^+$ rather than metal ions.

**Time affecting the absorption prosess:** Absorption rate of CCTS-TEPA was increased in the first hour of absorption prosess and then the rate was decrease gradually. The rate of absorption and desorption was balanced in the first hour. The absorption is a fast process.

**Study of Langmuir isotherm absorption:** The IR indicated that Cd(II) and Ni(II) was coordinated with CCTS-TEPA. The absorption motivity could influence absorption mechanism at some extent. Different absorption mechanism fitting absorption isotherm could measure the extent. Yuan *et al.*[11,12] studied crosslinked chitosan resin absorbed Cu(II), Ni(II) and Co(II). Using the Langmuir isotherm fitting the behaviour of crosslinked chitosan resin absorbed metal ions. The equation is:

$$C_e/Q_e = C_e/Q_m + 1/Q_m b \quad (1)$$

where, $Q_m$ is the resin monolayer saturation adsorption quantity. $C_e$ is balance concentration, $Q_e$ is balance adsorption quantity. The experiment fitting the absorption isotherm at 298 K, 308 K, 318 K.

It is founded that the behaviour of CCTS-TEPA absorbed Cd(II) and Ni(II) accord with Langmuir isotherm, as shown in Figs. 3 and 4 (Table-1).

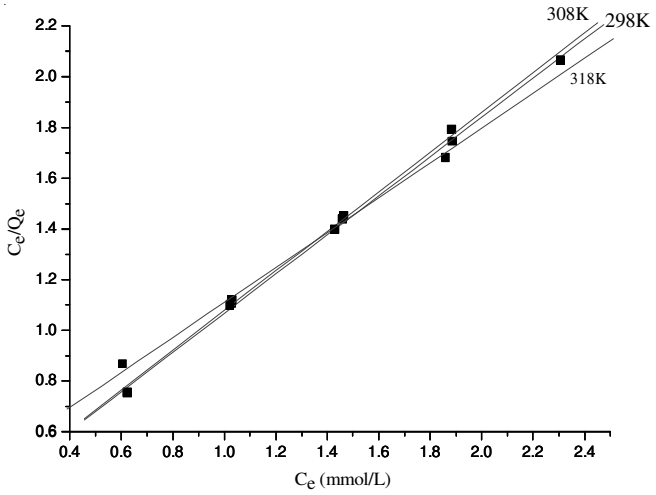


Fig. 3. Langmuir line at different temperatures of Cd(II)

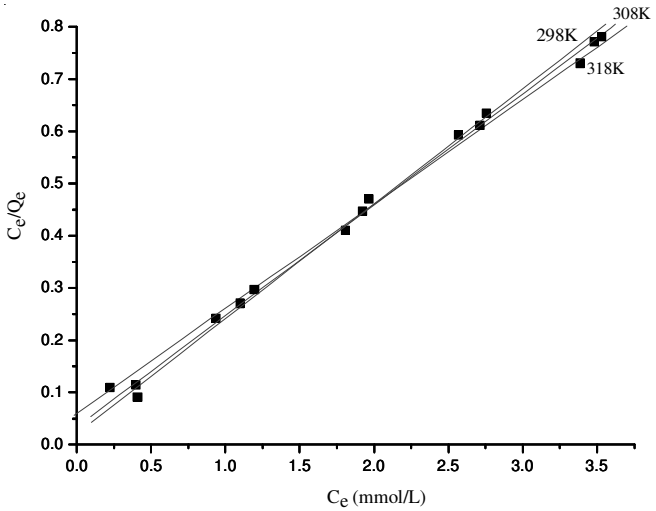


Fig. 4. Langmuir line at different temperatures of Ni (II)

TABLE-1
LANGMUIR ISOTHERM PARAMETERS FOR Cd(II) AND Ni(II) WITH CCTS-TEPA

| Temp. (K) | Fitting equations | b (L/mol) | $Q_m$ (mmol/g) |
|---|---|---|---|
| 298 Cd(II) | $C_e/Q_e = 0.7723C_e + 0.2958$ | 2.6108 | 1.2948 |
| 308 Cd(II) | $C_e/Q_e = 0.7815C_e + 0.2692$ | 2.9030 | 1.2796 |
| 318 Cd(II) | $C_e/Q_e = 0.6884C_e + 0.4214$ | 1.6336 | 1.4526 |
| 298 Ni(II) | $C_e/Q_e = 0.2202C_e + 0.02061$ | 10.6841 | 4.5413 |
| 308 Ni(II) | $C_e/Q_e = 0.2126C_e + 0.03382$ | 6.2862 | 4.6382 |
| 318 Ni(II) | $C_e/Q_e = 0.2003C_e + 0.06029$ | 3.3222 | 4.9926 |

**SEM analysis:** Fig. 5 is the SEM photo of CCTS-TEPA. It is not found holes in despite of high power.

Fig. 6 is the SEM photo of porous-CCTS-TEPA. The resin was pore-forming by PEG-2000. Obviously, there are many holes in the resin. It is make resin have large specific surface area.

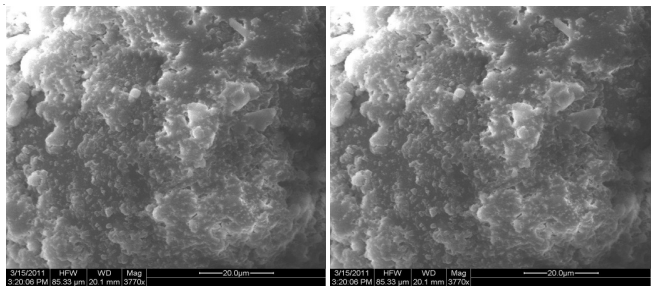

Fig. 5. SEM of CCTS-TEPA

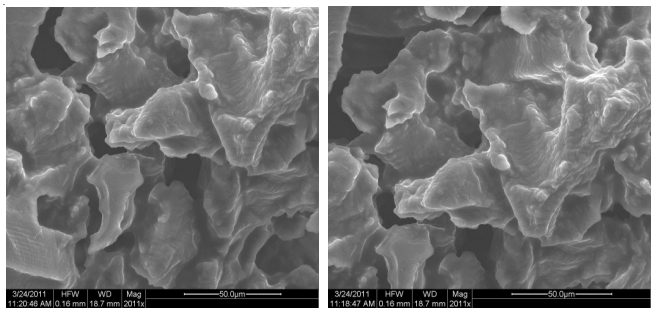

Fig. 6. SEM of porous-CCTS-TEPA

## Conclusion

Chitosan resin modified with tetraethylenepentamine (CCTS-TEPA) can absorb Cd(II), Ni(II). The absorption ability could get best in neutral solution. It could absorb Cd(II) and Ni(II) 123.54 mg/g and 262.50 mg/g respectively. The absorption behaviour is a fast process and accord with Langmuir isotherm. PEG-2000 as the Pore-forming agent, it could get porous-CCTS-TEPA, the diameter of the hole is 10 μm. It could absorb Cd(II) and Ni(II) 220.86 mg/g, 315.00 mg/g respectively. The absorption ability was obvious enhanced.

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