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## Synthesis of Covalent Organic Polymers for removing heavy metal ions with strong affinity

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# Synthesis of covalent organic polymers for removing heavy metal ions with strong affinity

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## INTRODUCTION

Demand for functionalized adsorbent that contains not only high surface area but also selectivity and recyclability has been increased for several decades. Especially, growing environmental problems such as water pollution introduced various application possibilities of functionalized adsorbents for pollutant treatment. Among the pollutant in water treatment system, heavy metal ion is non-degradable compound and it is difficult to be removed from polluted sites. Therefore, adsorption mechanism considered as a promise solution for removing heavy metal ions. Conventional technologies for heavy metal ion treatment have encountered a number of limitations. Activated carbon (AC) is commonly used for treatment due to its high porosity and low-cost, it has no functionality to uptake targeted pollutant selectively from heterogeneous circumstance. Besides, AC regeneration process consumes considerable amount of energy, hence, used-adsorbents tend to be incinerated rather than regenerated. Likewise, fulfilling only some conditions and ignoring others will lower the whole process efficiency during the treatment. Recently, porous polymers with various functionalities are suggested as a replacement of conventional methods to overcome several constraints. In this study, we designed functionalized covalent organic polymers (COPs) and synthesized it by bottom up methods to generate specific functionalities. By introducing functionalities into COPs we could enhance selectivity of adsorbent towards treatment target substances with sufficient surface area and porosity of adsorbent<sup>1,2</sup>. Surface area and porosity of functionalized COPs are analysed by Brunauer-Emmett-Teller (BET) surface area method and scanning electron microscope (SEM) and functionalities are confirmed by elemental analysis (EA), Fourier transform infrared (IR), and Thermo-gravimetric analysis (TGA). Heavy metal removal amount, isotherm, and kinetic were measured by Inductive coupled plasma mass spectrometry (ICP-MS) and Atomic adsorption spectroscopy (AAS). Here, we present functionalized COPs which carried sulfur functionality and achieved high selectivity towards heavy metal ions. All COPs showed thermal stability and low heat of adsorption which facilitating easy regeneration.

## MATERIALS AND METHODS

### Material

Cyanuric chloride and N,N-diisopropylethylamine (DIPEA), 4,4'-thiobisbenzenetrithiol, trimethylolpropane tris(3-mercaptopropionate), tetrahydrofuran, Dimethyl sulfoxide (DMSO), methyl alcohol, 1,4-dioxane and ethyl alcohol were purchased from Sigma-Aldrich. Chemicals are used as received.

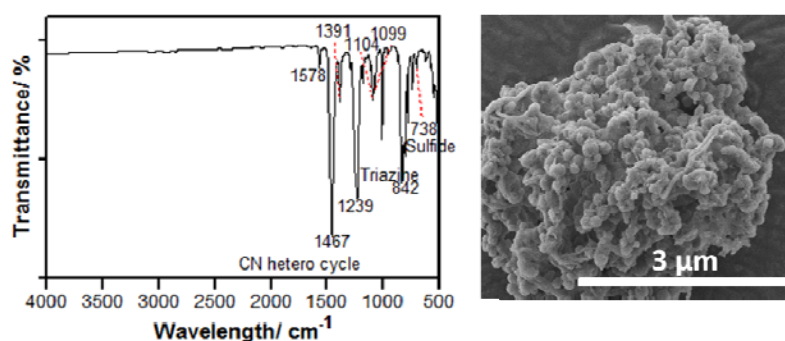
*Synthesis of Covalent Organic Polymer:* a) Under nitrogen atmosphere 4,4'-thiobisbenzenetrithiol and DIPEA were dissolved in 1,4-dioxane and placed into round bottom flask. After that cyanuric chloride were prepared as solution in 1,4-dioxane then

it was added into flask drop-wisely with continuous stirring at 15 °C. Mixture was stirred for 24 hours with three step temperature increases. After the reaction time, white precipitation was occurred and it was washed with 1,4-dioxane and ethanol over the period of 12 hours. Lastly, it was dried at room temperature under vacuum<sup>3</sup>). b) Polymerization was performed under ambient condition. Trimethylolpropane tris(3-mercaptopropionate) was added into DMSO and stirred vigorously for 24 hours at 80 °C. After gel-like precipitation observed, cool down the polymer and pour into the methyl alcohol. Centrifuge it and soaked in THF for 12 hours. Polymer was dried at 50 °C and 100 °C in a vacuum condition<sup>4</sup>).

*Metal adsorption test:* Prepare synthetic real condition water with specific heavy metal ions. In a conical PE tube, synthetic solution and covalent organic polymer were added together with calculated dose amount. The tubes were gently shaken and adjusted pH within a few minutes. We closed the cap tightly and shacked for 24 - 48 hours. Tubes were centrifuged and the solutions were collected to analyse their metal removal capacity.

## RESULTS AND DISCUSSION

From the result of IR, we could clearly observed sulphide group with triazine group which is intended to generate in the porous polymer. Also from SEM imaging, we found



the polymer contains small pores and the overall structure shows amorphous shape.

**Fig. 1. Structural analysis of covalent organic polymer. (Left: Fourier transform infrared graph of covalent organic polymer. Right: Picture from scanning electron microscope.)**

Metal adsorption test shows that covalent organic polymer with targeted functionalities achieved sufficient adsorption capacity and had selectivity on to heavy metal ions due to their chemical affinity between sulfur ions and heavy metal ions.

## CONCLUSIONS

In this study, we developed functionalized covalent organic polymer for removing heavy metal ions from the polluted water. We achieved sufficient adsorption capacity and high selectivity towards targeted heavy metal ions. Therefore, we found new candidate for efficient treatment way of heavy metal ion remove.

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