

# Application of Electron Beam to Environmental Conservation

*Koichi Hirota, Durga Parajuli, and Noriaki Seko*

*Environmental Polymer Group, Environmental and Industrial Material Research Division,  
Quantum Beam Science Directorate, Japan Atomic Energy Agency,  
1233 Watanuki, Takasaki, Gunma 370-1292, Japan.*

## Abstract

Lignin in Japanese cedar wood powder was extracted in the form of lignophenol and was modified with ethylenediamine and trimethylamine groups using Electron-beam technology. The functionalized lignophenol adsorbents were then studied for the recovery of precious metals: Au, Pt, and Pd from urban mine. From the batch test of mixture solution containing equal molar concentration of various metal ions, the sorbent was found to hold selectivity for Au(III), Pd(II), and Pt(IV) ions only with negligible sorption for other metal ions like Cu(II), Co(II), Fe(III), Ni(II), and Zn(II). The biomass sorbent is expected to be an excellent material for recovering the precious metal from urban mine.

## Introduction

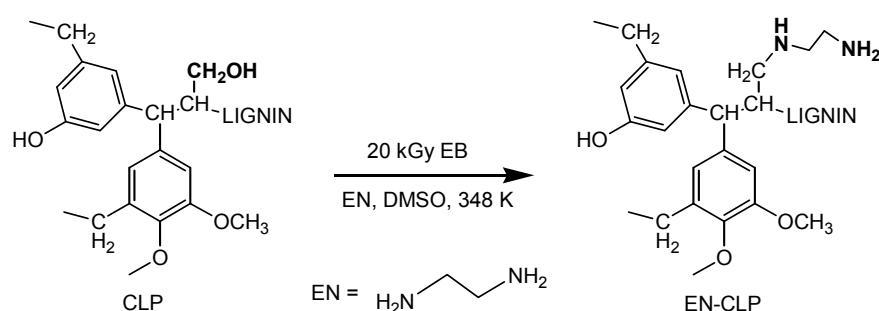
Precious metals like gold, platinum, rhodium, and ruthenium are essential materials for vehicles, electrical and electronic products, and catalysts. Japan is recently facing with daunting tasks for securing of resources because of high demand on resource by the BRICs, resource nationalism, and resource localization. Under these circumstances, the recovery of precious metals from electric and electronic wastes, so-called urban mine, is drawing much attention for the sustainable future. Conventional methods for recovery of precious metals from urban mine are solvent extraction and use of ion exchange resins. However, these methods have disadvantages of lack of required selectivity, huge chemical and energy requirement, and generation of toxic sludge or other waste products creating additional burden.<sup>1</sup> Biomass based sorbents is expected to be superior materials for recovering precious metals with lower capital cost and higher efficiency.<sup>2</sup> Despite holding better qualities, application of biomass-sorbents in industrial scale is rare. This is because of large amount of chemicals for their preparation and difficult functional modification. Ionizing radiation can effectively generate radicals to materials so that high functional modification of biomass is expected.

In the present work, wood derived lignin has been modified with ethylenediamine and tertiary amine group by electron-beam irradiation of the substrate, crosslinked lignophenol, followed by chemical reaction and their performance for the recovery of precious metals has been studied and the results are compared with that of chemically modified derivative.

## Experimental

### Preparation of lignophenol modified with ethylenediamine and trimethylamine

Lignophenol was prepared according to the phase separation method<sup>3</sup> using cedar wood powder generated while lumbering in Japan. It was then crosslinked with paraformaldehyde to obtain crosslinked lignophenol gel (CLP). In order to obtain ethylenediamine modified crosslinked lignophenol, the CLP matrix was irradiated by electron beam at a dose of 20 kGy and then directly treated with ethylenediamine in dimethylsulfoxide (DMSO) as shown in scheme 1. It is named as EN-CLP(EB). Chemically modified CLP with ethylenediamine group (EN-CLP(Chem)) was also prepared by following the same scheme without pre-irradiation for comparison of adsorption performance with EN-CLP(EB).



Scheme 1. Preparation of EN-CLP using electron beam

Trimethylamine modified CLP was prepared as: CLP was preirradiated with electron beam at a dose of 20 kGy was mixed with required volume of pyridine in a 3-necked flask kept in an ice-bath, under N<sub>2</sub>-atmosphere. With continuous stirring, thionyl chloride was added drop wise and once the addition of thionyl chloride was over, the mixture was stirred in the ice-cold condition for one hour and gradually heated to 75 °C. After 3 h, the mixture was cooled down, filtered, and washed with distilled water and dried at 70 °C in a convection oven. This chlorinated product, Cl-CLP was then treated with required volume of 30 % aqueous trimethyl amine at 90 °C. After 3 h, the mixture was cooled down, washed with 0.1 M HCl, 0.1 M NaCl, and finally washed with distilled water. The rigid mass obtained was dried and ground to 150 mesh size, and it was labeled as trimethyl amine type crosslinked lignophenol, TMA-CLP(EB).

### Adsorption test

The adsorption behavior of the EN-CLP(EB), EN-CLP(Chem) and TMA-CLP(EB) was tested batchwise by mixing 5 mL of 0.5 mM different metal chloride solutions at various hydrochloric acid concentrations with 10 mg sorbents. The sorbents at 10 mg was mixed with the solutions, followed by continuous shaking for 24 h at 303 K in a thermostatic shaking incubator. After filtration, the amount adsorbed was evaluated by measuring the residual metal concentration in the filtrate solution. Similarly, the adsorption isotherm was examined to evaluate the maximum loading capacities of the sorbents for Au(III), Pt(IV), and Pd(II).

## Results and discussion

### Adsorption performance of lignophenol modified with ethylenediamine

It is well known that e-wastes were treated with hydrochloric acid and aqua regia leaching to recover precious metals. Wastewaters generated during or after the recovery of metal ions are of high chloride concentrations and typically highly acidic with low concentration of metal ions. Aiming the recovery of valuable metals like gold, palladium, and platinum from this kind of industrial wastewaters that are highly acidic and consist of comparatively higher concentration of several other metal ions like Cu(II), Co(II), Fe(III), Ni(II), Zn(II), etc., the sorption behavior of EN-CLP was tested batchwise at varying hydrochloric acid concentrations. Figure 1 shows the adsorption of various metals on EN-CLP(EB) modified by electron-beam irradiation at varying hydrochloric acid concentration. The adsorption of Au(III) and Pt(IV) was more than 80 % even at 5 M hydrochloric acid medium. However, Pd(II) adsorption was decreased with an increase in acid concentration. Interestingly, the adsorption of other metal ions is near around zero. It was found that the sorbent of EN-CLP(EB) can be used for adsorption of gold and platinum even in highly acidic condition.

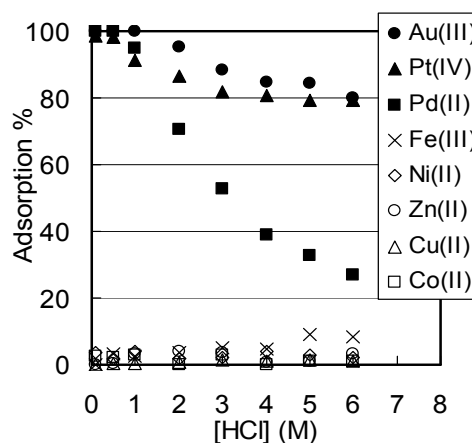


Figure 1. Adsorption behavior of EN-CLP(EB) for various metals in hydrochloric acid.

sorbent: 10 mg, solution: 5 mL of 0.5 mM each metal.

The sorption isotherms of gold, platinum, and palladium on EN-CLP(EB) and EN-CLP(Chem) were studied at 0.5 M hydrochloric acid condition and the data were analyzed in terms of Langmuir isotherm model. The Langmuir isotherm equation in linear form is given as equation 1.

$$\frac{C_e}{q} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \quad (1)$$

where,  $q$  is the equilibrium amount of metal ions loaded (mol/kg) on TMA-CLP,  $C_e$  is the concentration of metal ion remained in the solution (mol/L),  $q_{max}$  is the maximum loading capacity of TMA-CLP, and  $K_L$  is the Langmuir constant related to the energy of sorption. A plot of  $C_e/q$  as a function of  $C_e$  is shown in Figure 2. The lines for Au(III), Pt(IV), and Pd(II) are in linear agreement with a correlation coefficient of 0.98. From the relationship of the slope of the respective curves, the maximum loading capacity,  $q_{max}$ , for Au(III), Pt(IV), and Pd(II) were evaluated as 3.1, 2.3, and 0.85 mol/kg for EN-CLP(EB), and 2.4, 1.9, and 0.42 mol/kg for

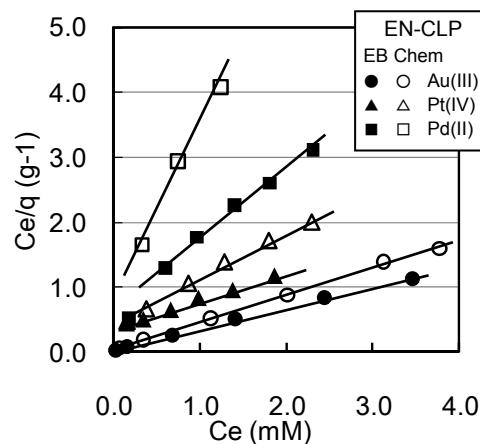


Figure 2. The Langmuir linear plot for the evaluation of maximum loading capacity.

sorbent: 10 mg, solution: 10 mL of 0.5mM metal in 0.5 M HCl.

EN-CLP(Chem), respectively. For Au(III) the capacity of irradiation modified adsorbent was 0.7 mol/kg higher than that of direct chemical modification, for Pt(IV) the difference was 0.4 mol/kg, and that of Pd(II) was almost double. These differences suggest that the degree of modification can be improved by the application of ionization radiation (electron beam in the present case).

### Adsorption performance of lignophenol modified with trimethylamine

As shown in Figure 3, the sorption of precious metals for TMA-CLP(EB) is almost quantitative throughout the whole experimental range whereas the sorption of other metal ions is nearly zero.<sup>4</sup> This adsorption performance is better than that of EN-CLP(EB) for the recovery of precious metals. Because ethylenediamine is a bulky moiety, the degree of its functional modification CLP is expected to be lower than that of trimethylamine. Also, the adsorption preference of EN-CLP(EB), a chelating sorbent, and TMA-CLP(EB), a quaternary amine sorbent, varies for metal ions exhibiting different aqueous chemistry with the variation of hydrochloric acid concentration.

The sorption isotherms of gold, palladium, and platinum on TMA-CLP(EB) were studied under 1.0 M hydrochloric acid condition as similar to those of EN-CLP. The obtained maximum loading capacity,  $q_{max}$ , for Au(III), Pt(IV), and Pd(II) were evaluated as 4.3, 1.3, and 0.74 mol/kg respectively. Table 1 shows the maximum loading capacities for TMA-CLP(EB) and EN-CLP(EB) under 1.0 M hydrochloric acid condition. Although the sorbents are modified with three different kinds of functional groups, the enhanced capacity of TMA-CLP, especially for Pd(II) and Pt(IV) by several folds is remarkable.

It is well known that metal ions like Au(III), Pd(II), and Pt(IV) form stable chloride anions of the form  $AuCl_4^-$ ,  $PdCl_4^{2-}$ , and  $PtCl_6^{2-}$ , respectively. Similarly, the amine group gets protonated in acidic medium and the positive charge is balanced by the coexisting anions, like chloride ion in the case of hydrochloric acid medium. In the present case, since hydrochloric acid of 0.5 M or more is the adsorption medium, the stable species of all the precious metals are anionic chloride complexes and the functional group of EN-CLP is abundant of protonated sites balanced by coexisting chloride ions. Hence, the anion exchange mechanism is the main adsorption process.

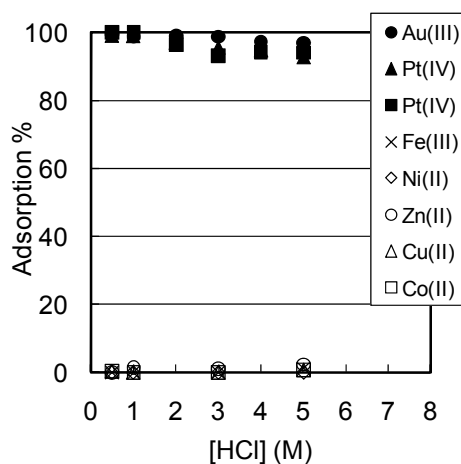


Figure 3. Adsorption behavior of TMA-CLP(EB) for various metals in hydrochloric acid.

sorbent: 10mg, solution: 5 mL of 0.5 mM each metal.

Table 1 Maximum loading capacity of lignin derivatives for precious metals in 1 M HCl

| Lignin Derivatives | Max. loading capacity (mol/kg) |        |        |
|--------------------|--------------------------------|--------|--------|
|                    | Au(III)                        | Pt(IV) | Pd(II) |
| TMA-CLP (EB)       | 4.3                            | 1.3    | 0.74   |
| EN-CLP (EB)        | 2.2                            | 0.91   | 0.31   |

### References

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