Reductive Adsorption of Gold(III) by Crosslinked Lignophenol

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The adsorption behavior of a crosslinked lignophenol gel for various metal ions from chloride medium was investigated. The gel was found to be only effective for the adsorption of Au(III) from weak to strong acidic medium. The analysis of XRD-spectrum and SEM-images of the adsorbent after adsorption revealed the formation of elemental gold by the reduction of the Au(III) ion. Such a result is promising for the development of a recovery system for gold from various industrial wastes.

Nowadays gold is in extensive use not only for jewelry but also in various electric and electronic devices. For example, about 0.2-kg gold is contained per 1 ton of mobile phones.[1] This amount is higher than the content in gold ore itself. Consequently, effective and economical recovery processes of gold should be urgently developed for its reuse and recycling in a sustainable society in the near future. The majorities of metal wastes containing valuable metals such as copper are finally collected at nonferrous metal smelters for copper and nickel where they are treated together with concentrates of these nonferrous metals.[2] Precious metals including gold are concentrated in anode slimes generated in the tank-house at the electrorefining step of the nonferrous metals. In order to separate and recover each precious metal, the anode slimes are totally dissolved in a hydrochloric acid leach liquor containing chlorine gas or hypochlorite to obtain a concentrated chloride solution, from which each precious metal is separated and recovered by means of solvent extraction and ion exchange.[3,4] According to the process commercially operated at Inco's Acton precious metal refinery, at the first step of the separation and recovery process, gold is separated by means of solvent extraction with dibutylcarbitol followed by reductive stripping with oxalic acid to obtain metallic gold.[5] Although this solvent has a high selectivity for gold, it is not totally satisfactory because of high water solubility which has significant cost considerations associated with the solvent loss which also causes wastewater treatment problems after solvent extraction which also incurs high cost. In the present work, we developed a novel separation process for gold using lignophenol prepared cheaply from wood powder. That is, we developed an innovative recovery process for gold from various wastes including spent mobile phones by using wood waste as a typical biomass waste.

For the preparation of lignophenol, wood powder generated in the lumbering of Japanese cedar trees in Miyazaki, Japan was used. The wood powder was first made extractives-free by stirring it with 1:2 v/v mixtures of ethanol and benzene. Then, lignin modified with phenol, lignophenol, was extracted according to the phase separation method developed by Funaoka.[6] The product thus obtained was washed with diethyl ether and then crosslinked with paraformaldehyde. The adsorption behavior of the crosslinked lignophenol gel was tested batchwise. 15 mL of 0.2 mM ($\mathrm{M} = \mathrm{mol\,dm^{-3}}$) of different metal chloride solutions at various hydrochloric acid concentrations were mixed with 20 mg of the adsorption gel followed by continuous shaking for 24 h at 30 °C in a thermostatic shaking incubator. The concentrations of the metal ions before and after adsorption were measured using a Shimadzu model AA-6650 atomic absorption spectrophotometer whereas tin concentrations were measured by using a Shimadzu model ICPS-100 III ICP-AES spectrometer. The initial and equilibrium hydrochloric acid concentrations were measured by titrating with standard sodium hydroxide solution using phenolphthalein as an indicator. The X-ray diffraction spectrum was recorded using a Rigaku RINT-8829 X-ray diffractometer while the SEM images were recorded using a JEOL model JSM 5200 scanning microscope under 25-kV acceleration voltage.

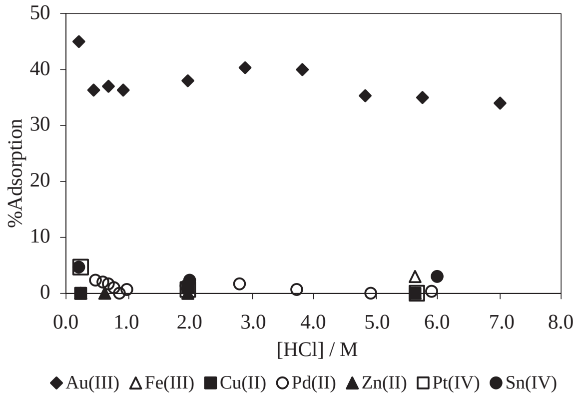


Figure 1. Plot of % adsorption of different metal ions on crosslinked lignophenol as a function of hydrochloric acid concentration. Initial concentration of metal ions = 0.2 mM, weight of adsorbent = 20 mg, shaking time = 24 h, temperature = 30 °C.

In the adsorption test for Au(III), Cu(II), Fe(III), Pd(II), Pt(IV), Sn(IV), and Zn(II), the crosslinked lignophenol gel was found to be effective only for Au(III), as shown in Figure 1. This shows that the gel is almost completely inert towards ferric, cupric, zinc, and stannic ions, which are among the major contaminants of gold. Also, in the adsorption test for a mixture of Cu(II) and Au(III) prepared in different concentrations of hydrochloric acid, a similar result was observed for gold whereas copper was not adsorbed at all. Such a high selectivity towards gold as observed in this work has not been reported to date.

Figure 2 shows the adsorption isotherm of gold, which exhibits a Langmuir type adsorption with a remarkably high maximum uptake capacity of about 1.92 mol per kg dry weight of the gel. With reference to the XRD spectrum of the adsorption gel

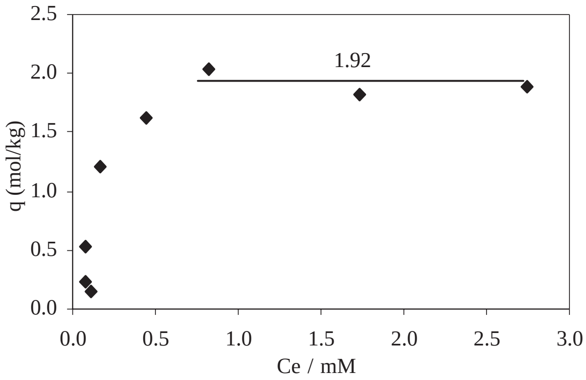


Figure 2. The adsorption isotherm of Au(III) ions on crosslinked lignophenol. [HCl] = 0.5 M, weight of adsorbent = 20 mg, shaking time = 24 h, temperature = 30 °C.

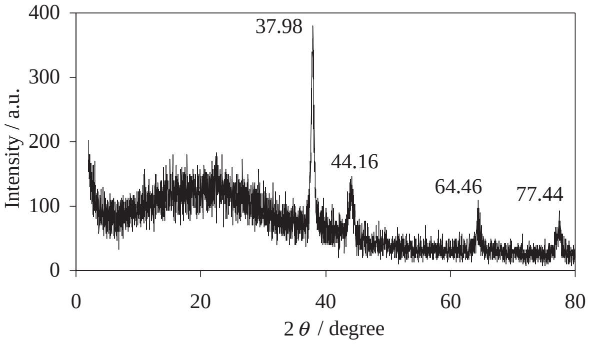


Figure 3. The XRD-spectrum recorded for the crosslinked lignophenol after the adsorption of Au(III).

after adsorption, shown in Figure 3, the adsorption process is confirmed to be accompanied by the reduction of auric ion to metallic gold. All four peaks at different 2θ values precisely match that of gold which reveals the presence of metallic gold in the sample. On analyzing the SEM images of the gel after adsorption (Figure 4a and 4b), we observed very fine gold particles of significantly different shape ranging from 10 to 50 µm scattered on the surface of the adsorbent. This means the metallic gold species are neither in the cage of the gel matrices nor in the bonded structure. This observation intensified the possibility of collection of gold particles even from a micro concentration level in strongly acidic to less acidic medium. In contrast to most of the commercially operated adsorption and solvent extraction systems, the crosslinked lignophenol gel does not need any foreign reducing agents in order to recover gold species in metallic form. Because lignin is one of the most abundant bioresources, which can be easily prepared from wood by means of the phase separation process, its use in the recovery of valuable metal in fine metallic form looks very practical. By using the technology described in this paper, gold free from impurities can be easily and economically produced.

Many circumstances are considered to be responsible for the reductive adsorption of Au(III). One is, the auric ion itself is a good oxidizing agent with a standard reduction potential of

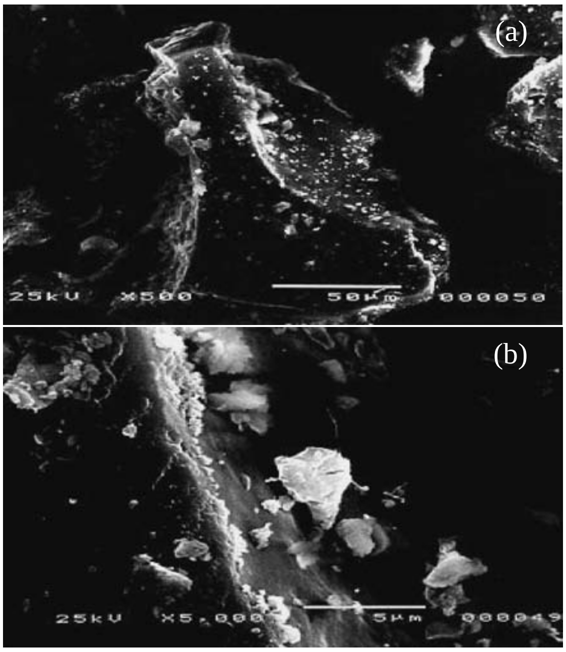
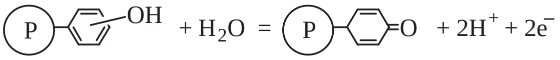


Figure 4. SEM images of the crosslinked lignophenol recorded after the adsorption of Au(III). (a) 500× magnification and (b) 5000× magnification; acceleration voltage = 25 kV; scale = 50 and 5 µm, respectively.

+1.40 V.[7] Another is, the presence of a large number of phenolic and polyphenolic hydroxy groups along with carbonyl groups which tend to oxidize in aqueous medium in the presence of certain metal ions, as shown in Eq 1, for example.[8] Hence, a mutual electron transfer mechanism is proposed to occur, thus establishing the redox system that provides electrons for the reduction of Au(III) as shown in Eq 2.



(1)

$$Au^{3+} + 3e^{-} = Au^{0} \qquad (2)$$

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