

Recovery and Separation of Precious Metals Using Waste Paper

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An adsorption gel was prepared from waste paper by immobilizing iminodiacetic acid so as to investigate its adsorption behavior for various metal ions from chloride media. The gel was found to be selective for Au^{III} and Pd^{II} over Pt^{IV} and other base metal ions including Cu^{II} , Fe^{III} , Ni^{II} and Zn^{II} at varying concentrations of hydrochloric acid. Moreover, Au^{III} was reduced by the gel giving rise to clearly recognizable beautiful elemental gold particles which was confirmed by means of the XRD-spectrum and SEM-images of the adsorbent after adsorption. This result has increased the prospect for mutual separation of Au^{III} and Pd^{II} from coexisting Pt^{IV} and base metals.

The demand for precious metals like gold, palladium, and platinum is ever increasing because of their newer and broader applications in various sectors such as manufacturing of electronic and electrical devices, automobile catalysts, and biochemical applications, i.e., pharmaceuticals, which have led to the increase of the price of precious metals over the past years. In addition, diminishing quality of the available mined ores and the environmental degradation associated with mining have considerably raised their production cost. Under these circumstances, a world-wide interest in their recovery from secondary resources has emerged.¹ From the viewpoint of sustainable development, this should be taken as a positive note as it will help to reduce the alarming level of electrical and electronic wastes in the developed countries produced as a result of the cutthroat competition in the market of PCs, mobile telephones, and entertainment electronics.

Various processes are in practice currently, and many alternatives have been reported in the literature for the effective and efficient recovery of precious metals.² Generally precious metals contained in anode slimes generated during electrorefining of nonferrous metals are totally dissolved in hydrochloric acid containing chlorine gas to obtain a concentrated chloride solution, from which each precious metal is separated and recovered by means of solvent extraction and ion exchange.³ However, various drawbacks such as slow kinetics, high cost, and the release of environmentally unacceptable chemicals in waste streams are associated with the solvent extraction technique. On the other hand, the application of commercially available ion-exchange resins and chelating resins is limited owing to their nonselective nature and low uptake capacity for precious metals.

In this context, we have investigated the utilization of waste biomasses as sorption active materials for the recovery of valuable metals from waste water. In our previous study, a recovery process for gold from chloride media using an adsorption gel generated from wood, lignophenol, as well as persimmon peel gel has been investigated.⁴

It is evident that tons of waste paper is being generated in various forms everyday. Unlike pure cellulose, amorphous matrix of paper makes it easier for chemical modification. In this paper, from the viewpoints of the effective use of waste paper

and the recovery of precious metals from various secondary resources, we have investigated the selective recovery of precious metals using chemically modified waste paper.

The detailed process for the preparation of the gel has been published elsewhere⁵ and can be summarized as follows: waste newsprint paper was pretreated with a concentrated solution (20%) of NaOH for a few hours followed by washing and drying. It was further treated by chlorination with thionyl chloride in the presence of pyridine. At the same time, iminodiacetic acid was converted to diethyl iminodiacetate by treatment with ethanol saturated with HCl gas. The reaction between the chlorinated waste paper and diethyl iminodiacetate in acetonitrile in the presence of K_2CO_3 and subsequent hydrolysis of the product with 1 M ($\text{M} = \text{mol dm}^{-3}$) NaOH in ethanol and 0.1 M HCl in turn yielded the final product.

For the adsorption study, test solutions of various metal ions were prepared by using analytical grade salts or acids of the respective metals. To study the adsorption behavior of waste paper gel batchwise, 15 mL of 0.2 mM of different metal chloride solutions at varying hydrochloric acid concentrations was individually mixed together with 20 mg of the adsorption gel followed by continuous shaking for 24 h at 30 °C in a thermostatic shaker. For the isotherm study, the concentration of the metal ion was varied while keeping the gel weight and solution volume constant. The concentrations of the metal ions before and after adsorption were measured by using a Shimadzu model ICPS-8100 ICP/AES spectrometer. 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 an acceleration voltage of 15 kV.

The adsorption behavior of iminodiacetic acid type of modified waste paper gel for a number of base and precious metal ions in hydrochloric acid was studied batchwise. As shown in Figure 1, the waste paper gel was found to be selective only for Au^{III} and Pd^{II} , which suggests that the gel not only

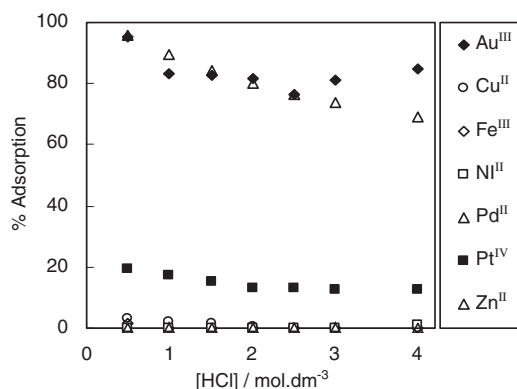


Figure 1. Adsorption of different metal ions on waste paper gel as a function of hydrochloric acid concentration.

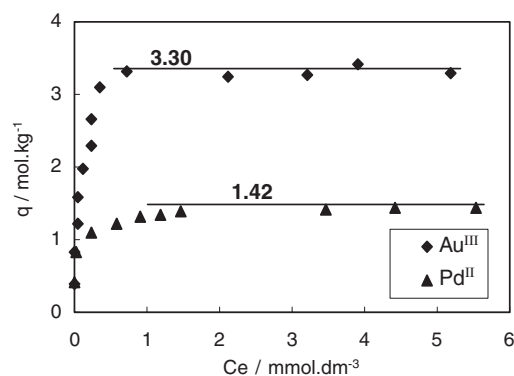


Figure 2. The adsorption isotherms of Au^{III} and Pd^{II} ions on the waste paper gel. [HCl] 1 M, weight of adsorbent 20 mg, volume of the solution 15 mL, shaking time 60 h, temperature 30 °C.

discriminates against Pt^{IV} but is also inert toward base metals such as Fe^{III}, Cu^{II}, Zn^{II}, and Ni^{II} which are major contaminants of gold and palladium. Taking account of the fact that most of these metal ions coexist in various industrial waste solutions and leach liquors, the result is promising for the selective recovery of Au^{III} and Pd^{II} from any base metal and most interestingly even from Pt^{IV}.

Since the gel has exhibited strong adsorption only for Au^{III} and Pd^{II}, the adsorption isotherm study was carried out for these two metal ions. As is evident from Figure 2, the gel exhibits a remarkably high adsorption capacity of 3.3 and 1.42 mol kg⁻¹ dry weight of the gel for Au^{III} and Pd^{II}, respectively, in 1 M hydrochloric acid medium. This difference in capacity for Pd^{II} and Au^{III} is ascribed to the reduction of the Au^{III} ion to the elemental form during adsorption as will be described in detail subsequently.

In addition, considering the practical importance of the selective adsorption of precious metals in stronger acidic medium, it was preferred to observe the loading capacity of the waste paper gel at higher concentrations of hydrochloric acid. Adsorption isotherm study for Au^{III} and Pd^{II} was carried out also at 2, 3, and 4 M hydrochloric acid media, and the respective values are given in Table 1. Regardless of the acid concentration, comparable maximum loading capacities were observed for Au^{III}, and a slightly decreasing order was found for Pd^{II}. This result can be correlated well with that of Figure 1 where the adsorption percentage of Au^{III} at higher acidic medium is only slightly lower than at 1 M and the values are in decreasing trend for Pd^{II}. Nevertheless, the stable performance of the gel with comparably high adsorption capacities at any concentrations of hydrochloric acid provides strong advantage for the real life application.

In order to confirm the reduction of Au^{III} to Au⁰, the XRD spectrum of the gel was taken after the adsorption of Au^{III}. Sharp peaks at 2θ values of 38.24, 44.46, 64.6, and 77.68 degrees were observed which belong to the metallic gold. The observation suggests the reduction of the Au^{III} ion to the elemental form during adsorption. This fact was further reinforced from the SEM image of the gel taken after the adsorption of Au^{III} as shown in Figure 3a in which very fine aggregated particles of gold (gray complexion) with various shapes are distinct. Also, Figure 3b shows a photograph of the sample solution and the gel in a glass vessel after shaking, from which the aggregated gold particles floating on the surface of the HCl solution can be seen. It was also observed that these aggregates became larger

Table 1. Maximum adsorption capacities of waste paper gel for Au^{III} and Pd^{II} at different concentrations of hydrochloric acid

[HCl] (mol·m ⁻³)	1	2	3	4
Au ^{III} (mol·kg ⁻¹)	3.30	3.09	3.06	2.98
Pd ^{II} (mol·kg ⁻¹)	1.42	1.25	1.12	0.95

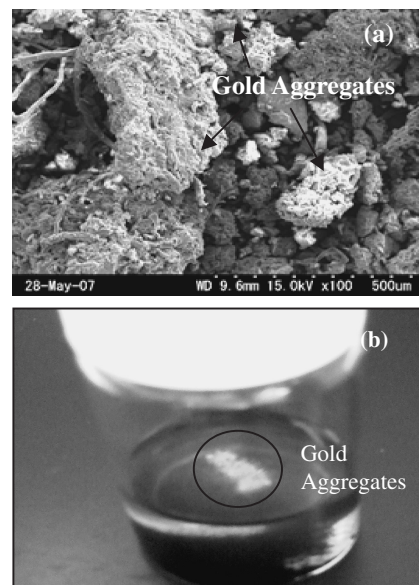


Figure 3. (a) SEM image of the waste paper gel after the adsorption of Au^{III} at 100× magnification. Acceleration voltage: 15 kV. (b) Photograph of gold aggregates floating on the surface of HCl solution after adsorption.

and denser with time and fell down to the bottom of the solution in a few hours. These results prove that gold particles formed by the reduction show a tendency to detach from the gel surface and form clean aggregates. This kind of observation was also found in our previous study.³

High selectivity of the waste paper gel for Au^{III} and Pd^{II} and subsequent reduction of the Au^{III} ion to the metallic form leading to its physical separation from the gel matrix has given a new insight not only into the recovery and isolation of precious metals but has also demonstrated potential application in the mutual separation of precious metals.

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