Recovery of precious metals by using chemically modified waste paper

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Waste newsprint paper was chemically modified with *p*-aminobenzoic acid to prepare a sorption active gel. This gel proved useful for the selective uptake of gold, palladium and platinum over other coexisting metal ions such as copper, nickel, zinc and iron. A remarkably high capacity for Au(III) was observed together with a moderate uptake of Pt(IV) and Pd(IV). Furthermore, Au(III) was reduced to elemental gold which formed aggregates. A high percentage recovery of the precious metal ions (85–95%) and regeneration of the gel was attained by using a mixture of 0.15 M thiourea and 1 M HCl. Repeated cycles of uptake and elution by using a column packed with this new sorbent indicated that the gel is suitable for industrial application in continuous mode.

Introduction

Paper is an important part of our everyday life and also one of the various cellulosic biomass wastes generated in voluminous amounts in various fields. It is not a surprise that paper can be recycled and reused as paper only for a limited number of times due to the shortening of fibre length and lowering of the fibre tensile strength at each successive step of recycling. As a result, it loses most of its value and becomes worthless garbage which occupies 30–40% of landfill sites in developed countries.[1] Also, the fibres left over from the process of paper production, which contain over 70% of pure cellulose, have been usually discarded with the wastewater in amounts of several thousands tonnes a year, thus presenting a significant environmental pollution problem.[2] Consequently, from the perspectives of both environment and economy, efforts are being made to reclaim value from this cheap biomass in the form of energy and advanced functional materials by the effective use of its unique characteristics.[3]

At the same time, mining of precious metals has been scaled up worldwide owing to the ever increasing demand of these metals in recent decades. During metal refining, large volumes of aqueous by-products are produced, which contain a substantial proportion of high-value metals, along with other metals. These precious metals are discarded, while the discharge of coexisting toxic metals leads to the contamination of the aqueous system.

Conventional methods for the removal or recovery of such low concentrations of dissolved metal ions from wastewaters are solvent extraction, chemical precipitation and ion exchange (using synthetic ion exchange resins). Such methods suffer from significant disadvantages such as incomplete metal removal, high capital costs, large chemical and/or energy requirements, and generation of toxic sludges or other waste products that require disposal.[4] These drawbacks have given rise to the need for more economical and effective methods for the recovery of metals from wastewaters.

In this context, sorption processes using low cost and widely available biomass materials (living or dead) represent an interesting alternative as they have shown great promise for the treatment of pollutants in industrial effluents. More recently, materials like fungal, algal and bacterial biomass as well as alginate and chitosan have been extensively studied for their remarkable and high sorption capacities.[5,6] From an environmental viewpoint, the use of biomass materials is more favourable because it is easier to recover the loaded metal ions from biomass either by elution or by incineration. Sorption by waste paper, in particular, can be a promising alternative since it acquires a special property for binding and accumulating metals even at trace levels, like other biomasses. In previous work, we have successfully utilized modified waste paper for the preconcentration and separation of heavy metal ions.[3]

Unlike commercially available cellulose, waste paper cellulose is highly amorphous and hence is more accessible to chemical modification. A high degree of functionalization can therefore be achieved, even under normal laboratory conditions. Generally, amine ligands are known to effectively coordinate to platinum group metals and are applied mainly as anion exchange extractants in hydrometallurgical processes.[7] Castro *et al.* have immobilized *p*-aminobenzoic acid on microcrystalline cellulose to test the sorption of some metal ions *viz.* Cu(II), Pb(II), Zn(II), Cd(II) and Ni(II) in a pH range of 1–7.[8] In the present study, we have investigated a waste paper gel modified with the same group for the sorption of precious and other metals from varying concentrations of hydrochloric acid.

Results and discussion

Characterization of the gel

The degree of immobilization of the *p*-aminobenzoic acid group onto the waste paper was analyzed by means of FTIR and elemental analysis. FTIR (KBr): Waste paper; ν 3420 (O–H), 2913 (C–H), 1164 (C–O–C), 899 (C_1-H), 1051 (C–O);

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and PAB-paper gel; ν 3400 (O–H, N–H broad), 1639 (C=O), 1513 (C=C), 1278 (aromatic ring deformation), confirms the introduction of the *p*-aminobenzoic group onto the paper matrix. Elemental analysis: (Found: C, 33.16; H, 3.35; N, 3.35. Calc. for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.34; N, 4.98%) gives the degree of substitution as 68% which accounts for 2.39 mol of functional group per kg of the paper.

Sorption kinetics

The sorption kinetics of the PAB-paper gel was studied at 30 °C. Fig. 1 shows the rate of sorption of Au(III), Pt(IV) and Pd(II). As is evident from this figure, in the case of Pt(IV), equilibrium was reached within 5 h, whereas, in the case of Au(III) and Pd(II), it took a longer time (about 24 h). The kinetic data in the inset depicts the sorption% in 0–2 h. It is clear from the figure that almost 80% of the Au(III) and Pd(II) ions present in the solution are sorbed within 2 h whereas only about 60% of Pt(IV) was sorbed in the same time. In short, although the total equilibrium time is longer compared to ion exchange resins, the sorption rate at the beginning is quite appreciable. However, for determining the sorption capacity, a longer period (50 h) was adopted, the rationale for which will be justified in a later section.

Uptake experiments at varying HCl concentrations

The sorption behaviour of the PAB-paper gel for various metal ions is shown in Fig. 2(a), from which it is clear that all three precious metal ions *i.e.* Au(III), Pt(IV) and Pd(II) were quantitatively sorbed over the whole range of hydrochloric acid concentrations, whereas the gel showed no affinity for metals such as Fe(III), Ni(II) and Zn(II). Some Cu(II) was sorbed at low HCl concentrations but sorption was negligible at higher concentrations of HCl. A study on the metal uptake behaviour of unmodified waste paper was also carried out and the degree of sorption was found to be insignificant (result not shown).

In order to compare the results observed for the PAB-paper gel, similar experiments were carried out by using three different types of commercial ion exchange resins containing amine groups. Although an exact analogue of the PAB paper gel was not available, Diaion WA30 (dimethyl amine), Diaion WA21 (polyethylene poly amine), and Diaion CR11 (iminodiacetic acid) were taken as representative amine-containing resins. The selectivity shown by Diaion WA30 was found to be poorer than that of the waste paper gel as reported in our previous study.[9] The results observed for Diaion WA21 and Diaion CR11 are given in Fig. 2(b) and (c), respectively. The performance of Diaion WA21 was found to be poorer than that of the paper gel, whereas, in the case of Diaion CR11, only gold selectivity was significant with less sorption affinity for Pt(IV) and Pd(IV). However, besides the difference in selectivity, taking account of the origin of waste paper gel as an easily available biomass waste with little chances for further recycling and the simple steps required for modification, it certainly possesses stronger scope for use as an alternative sorption material.

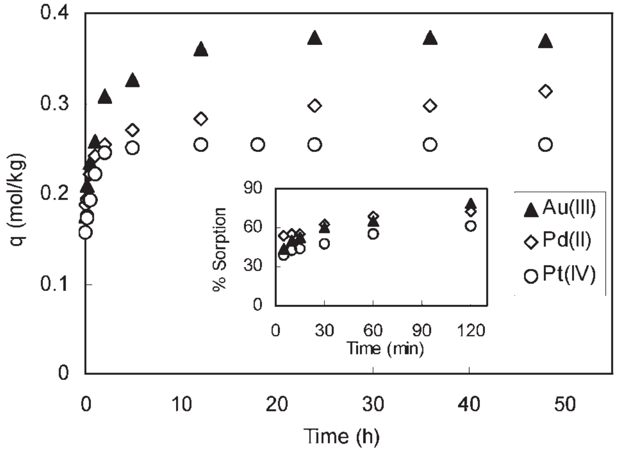


Fig. 1 Sorption kinetics of metal ions using the PAB paper gel. Initial concentration of metal ions = 0.5 mM, [HCl] = 1 M, wt. of gel = 20 mg, temperature = 30 °C.

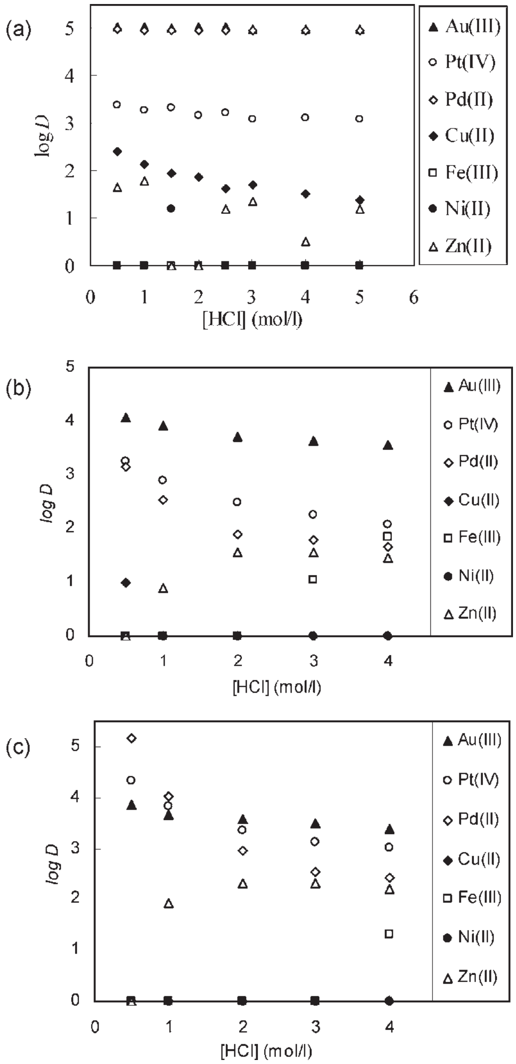


Fig. 2 Sorption of various metal ions over a range of hydrochloric acid concentrations [D = (mol M^{n+}/kg of dry gel)/mol M^{n+}/l of solution)]. (a) PAB paper gel, (b) Diaion CR 11, and (c) Diaion WA 21. Initial concentration of metal ions = 0.2 mM, wt. of gel = 20 mg, shaking time 24 h, temperature = 30 °C.

Sorption mechanism

Since all the sorption tests were conducted in hydrochloric acid medium, it is important to note the most stable forms of the metals under discussion in acidic chloride media. The species distribution diagrams for Au(III), Pd(II) and Pt(IV) are shown in Fig. 3.[10] It is clear from the figures that Au(III), Pd(II) and Pt(IV) exist mostly as anionic chloro-complexes such as $AuCl_4^-$, $PdCl_4^{2-}$ and $PtCl_6^{2-}$, respectively in the strong acidic conditions of the experiment. Because the PAB-paper gel has selectively sorbed only the precious metals, with no distinct sorption affinity for other metal ions, it is important to note the aqueous chemistry of the various other metal ions also in chloride medium. While the anionic chloride species of Au(III), Pd(II) or Pt(IV) exist over a wide range of chloride concentrations, metal ions such as Cu(II), Zn(II), Fe(III) and Ni(II) exist mostly as cationic or neutral species and the concentration of anionic chlorides is significant only at higher chloride concentration.[11] This dominance of the precious metal anions in the 1–4 M HCl concentration range almost certainly accounts for their selective sorption.

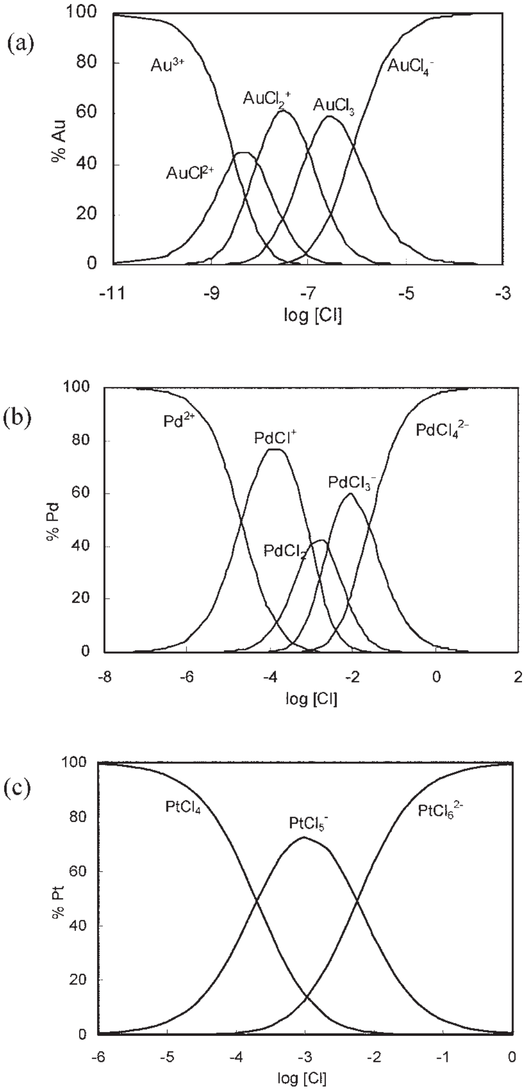


Fig. 3 Chemical speciation diagrams of Au(III), Pd(II) and Pt(IV) ions with respect to chloride concentration.

The amine group of the PAB-paper gel in hydrochloric acid medium is protonated as described by eqn (1). Hence, the sorption of metal chloro-complexes takes place according to the anion exchange reactions as expressed by eqn (2) for Au(III) and eqn (3) for M = Pd(II) and Pt(IV), where the coordination numbers of these metal ions (four for Au(III) and Pd(II) and six for Pt(IV)) are satisfied by coexisting Cl^- ions.

$$RNHC_6H_4COOH + H^+{\cdot}Cl^- \leftrightarrow RNH_2^+(C_6H_4COOH){\cdot}Cl^- \qquad (1)$$

$$RNH_2^+(C_6H_4COOH){\cdot}Cl^- + AuCl_4^- \leftrightarrow RNH_2^+(C_6H_4COOH){\cdot}AuCl_4^- + Cl^- \qquad (2)$$

$$2(RNH_2^+(C_6H_4COOH){\cdot}Cl^-) + MCl_n^{2-} \leftrightarrow (RNH_2^+(C_6H_4COOH))_2{\cdot}MCl_n^{2-} + 2Cl^- \quad (M = Pd(II)/Pt(IV)) \qquad (3)$$

Sorption isotherms

Since the PAB-paper gel has shown strong sorption affinity for Au(III), Pd(II) and Pt(IV), its sorption isotherm was examined. As shown in Fig. 4, sorption increases with increasing metal concentration at low concentration while the isotherms tend to approach constant values corresponding to each metal species at high concentration, *i.e.* a plateau region, suggesting a typical Langmuir type sorption. From the constant values in the plateau region, the maximum sorption capacity for Au(III) was evaluated as 5.1 mol kg^{-1} (1005 g/kg of dry gel) in 1 M hydrochloric acid medium. Although some studies on sorption on biomasses have reported higher capacities for Au(III) in acidic medium, such a high capacity has been rarely observed.[9,12–16] This high capacity of the PAB-paper gel can be applied for the preconcentration and recovery of gold contained in wastewater generated by metal refineries or other industries. Likewise, the gel has shown about 1.5 mol kg^{-1} (160 g/kg of the dry gel) and 0.5 mol kg^{-1} (98 g/kg of the dry gel) loading capacity for Pd(II) and for Pt(IV), respectively.

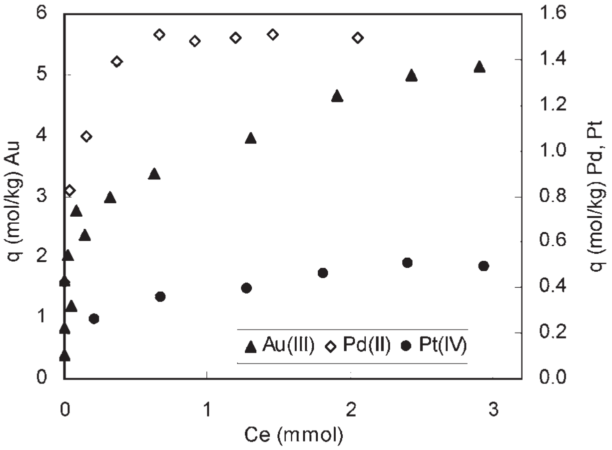


Fig. 4 The sorption isotherms of Au(III), Pd(II) and Pt(IV) on the PAB-paper gel. *Ce* = Equilibrium concentration, *q* = amount of metal uptake, [HCl] = 1 M, wt. of gel = 20 mg, vol. of solution = 15 ml, shaking time = 50 h, temperature = 30 °C.

Table 1 Comparison of the loading capacities for Au(III), Pd(II) and Pt(IV) with other sorbents

	Loading capacity/mg g^{-1}			
Sorbent	Au(III)	Pd(II)	Pt(IV)	Ref.
Ethylenediamine modified crosslinked lignophenol gel (EN-Lignin)	607	22.7	105	9
Primary amine modified crosslinked lignophenol gel (PA-Lignin)	384	40.4	43	9
Lysine modified crosslinked chitosan	70.3	109	129	12
Glycine modified crosslinked chitosan resin	170	120	122	13
2-Mercaptobenzothiazole-bonded silica gel	4.5	18	6.5	14
Poly(vinyl benzyl chloride–acrylonitrıle–divinylbenzene) modified with tris(2-aminoethyl)amine	190	280	245	15
Amberlite IRC 718	136	58.5	66.3	16
PAB-paper gel	1004	160	98	This work

Although these values are much lower than that for Au(III), compared to the recovery of Pd(II) and Pt(IV) by other biomass wastes, as shown in Table 1, the capacity is appreciable.

Obviously, the sorption capacity of the gel for Au(III) was much higher than the functional group density of the amino group immobilized on the gel. The high sorption capacity of the gel can be explained in terms of the formation of clearly visible gold particles on the surface of the test solution. During or presumably after sorption, the gel reduced gold ions to elemental gold particles. XRD spectra of the gel were taken before and after the sorption to confirm the presence of elemental gold. Additionally, sorption tests for test solutions containing all three precious metals were carried out to understand the reducing effect of the gel on coexisting metal ions. However, only peaks belonging to elemental gold were observed, as shown in Fig. 5(a). This proves that only Au(III) undergoes subsequent reduction after being sorbed on the gel matrix and the other metal ions do not change their oxidation states. From this difference, it is clear that the sorption of palladium and platinum is purely an ionic interaction, whereas for gold, the ionic interaction is followed by subsequent reduction to the elemental form. In addition, no such peaks for elemental gold were observed in the case of the previously mentioned ion exchange resins under the same test conditions, indicating that the reduction of Au(III) to its elemental form does not occur with the commercial resins (figure not shown). Fig. 5(b) shows the SEM image of the PAB-paper gel after gold sorption. The gold clusters of polygonal (mostly hexagonal) shape on the surface of the gel explain the fact that the reduction of gold to the elemental form leads to the separation of adsorbed gold from the gel matrix to form the elemental gold aggregates. The sorption–reduction and aggregation of gold particles allows further sorption of Au(III) ions from the solution resulting in the high loading capacity for gold.

As the high sorption ability of the PAB-paper gel for Au(III) is associated with the reduction of the gold ion to the elemental form, certain changes in the electromotive force (emf) is also expected during the sorption process. A change in solution potential in relation to the sorption kinetics was observed as shown in Fig. 6. It is clear from the figure that within 5 h almost 90% of the metal ions are sorbed and the oxidation reduction potential (ORP) begins to fall significantly at this point. The reduction process seems to be slow and continuous; lasting for several hours till it reaches a minimum value.

Reduction mechanism

It is well known that Au(III) has a higher oxidation reduction potential compared to Pt(IV) and Pd(II) which makes it a powerful oxidising agent with a tendency to reduce to Au(0) in aqueous systems. In hydrochloric acid medium the oxidation reduction potential (ORP) values for Au(III), Pt(IV) and Pd(II) have been reported as 1.002, 0.744 and 0.62 V, respectively, by Bard *et al.*[17] It is not easy to explain the reason why Au(III) is not reduced by amine type commercial anion exchange resins but is reduced in the presence of amine type biomass sorbents like the PAB-paper gel. Obviously the PAB-paper gel is not a unique case; we have already observed a few precedents for such a phenomenon in the past. In our previous work on cross-linked lignophenol as well as its aminated derivatives, we observed similar phenomena and the

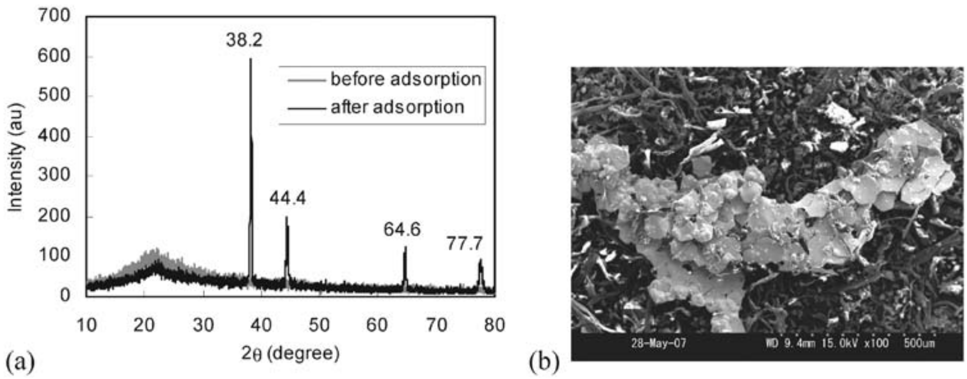


Fig. 5 (a) XRD spectrum of the PAB-paper gel taken before and after sorption of precious metals. (b) SEM images of the aggregated gold particles on the surface of the gel.

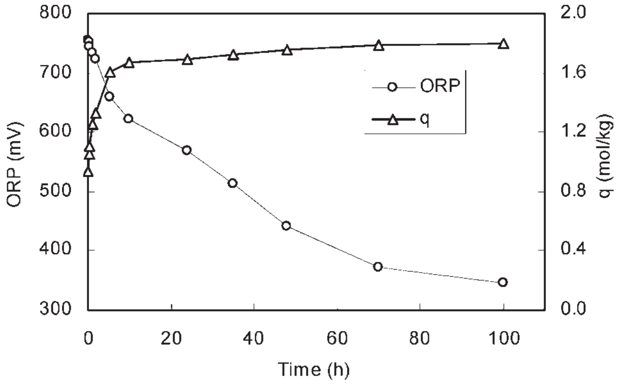


Fig. 6 The oxidation reduction potential (ORP) of the Au(III) solution in contact with the waste paper gel. Initial concentration of metal ions = 2 mM, [HCl] = 1 M, wt. of gel = 20 mg, temperature = 30 °C.

existence of the large number of phenolic and polyphenolic groups was concluded to be responsible for the reduction of Au(III).[18] Earlier, the reduction and accumulation of gold by various types of biomass such as alfalfa, natural condensed tannin, calcium alginate, brewery waste, algal biomass and dealginated seaweed waste has been reported in the literature, but unlike in our work, visual observation of fine gold particles on the surface of the solution has not been reported.[19] Reports of such instances in the case of cellulose and chitosan (original or modified) have not been found.

Although the presence of amine groups containing lone pairs of electrons as well as the electron rich benzene moiety may be responsible for the reduction, the exact mechanism of Au(III) reduction and its accumulation by the biomass is unknown and must be elucidated in future work by taking into account of the aqueous chemistry of gold ions and colloids. Park *et al.* explained the sorption-coupled-reduction of Cr(VI) to Cr(III) in terms of the oxidation of the aldehyde end group of cellulose to the corresponding carboxylic acid.[20] However, owing to the lack of any evidence of the oxidation of the cellulose matrix, it is difficult to interpret the mechanism in terms of the oxidation of the cellulose aldehyde in waste paper during the reduction of Au(III). Similarly, oxidation of biomass functional groups such as hydroxyl and carboxylic groups cannot be concluded without reliable proof.[21] In addition, an extensive report on Au(III) reduction by Richardson *et al.* using various types of monomeric and polymeric amines has stated that even spectroscopic methods such as NMR were not able to confirm the reduction mechanism.[22]

Column experiment: sorption and elution

Since the PAB-paper gel has shown selectivity for precious metals and a high sorption capacity for gold, a column test was carried out using a binary mixture of Au(III) and Cu(II) as the latter exists together with precious metals in real waste solutions. Fig. 7(a) shows the breakthrough profiles of a model solution containing a low concentration of Au(III) together with 10 times the concentration of Cu(II) after passing through the column packed with 0.1 g of the PAB-paper gel. It is clear from the figure that Cu(II) passes without being sorbed but Au(III) is completely sorbed for up to 40 h. However, saturation was not reached until 130 h due to continuous sorption and reduction.

Owing to the irreversible strong sorption of the chlorocomplexes of Au(III), Pd(II) and Pt(IV) on conventional anion exchange resins, the elution of loaded metal ions is inefficient in many actual cases.[23] To test the performance of the PAB-paper gel in this regard, the sorbed metal ions were eluted by using a mixture of 0.15 M thiourea in 1 M HCl. Almost complete recovery of Au(III) (~95%) was attained by this method with a preconcentration factor as high as 40 (Fig. 7(b)). Interestingly, the dissolution of fine gold particles in the acidic thiourea solution indicates not only the possibility of complete recovery of the loaded gold but also the suitability of the gel for regeneration and its repeated use. For further confirmation, a cycle test was carried out by passing a mixture consisting of 20 mg l^{-1} Au(III) and 100 mg l^{-1} Cu(II) through a column packed with 0.1 g of the gel and eluting the loaded metal ions with acidic thiourea. The results of the experiment are shown in Table 2, revealing that more than 90% of the sorbed gold was eluted each time.

In the same way, four consecutive sorption–elution cycle tests were conducted for a mixture containing Pt(IV) and Pd(II). The feed concentration of each metal ion was set at 20 mg l^{-1} for the first cycle. However in order to know the influence of higher concentrations of one metal over the other, in the

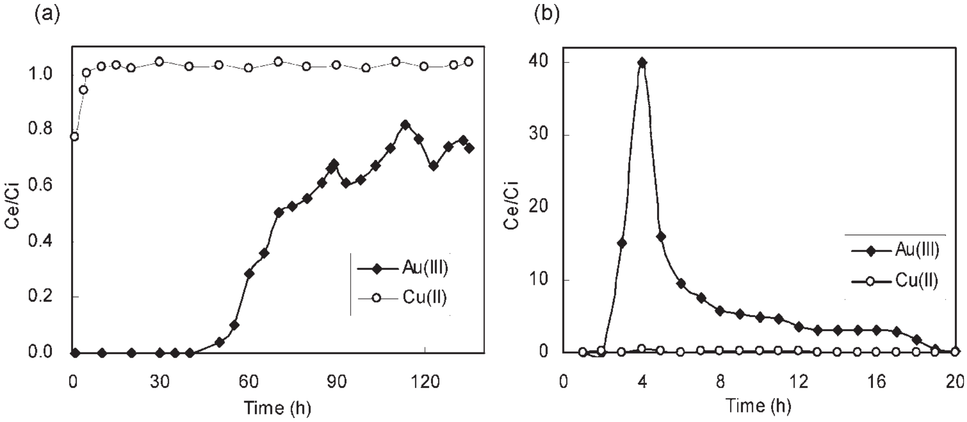


Fig. 7 (a) Breakthrough profiles of Au(III) and Cu(II). (b) Elution profile. [*Ci* is the initial concentration of the metal ions and *Ce* is the metal ion concentration of the effluent solution.] Feed concentration: Cu(II) = 100 ppm, Au(III) = 20 ppm, flow rate = 6.5 ml h^{-1}, eluent = 0.1 M thiourea in 1 M HCl.

Table 2 Performance of the PAB-paper gel in consecutive adsorption–elution cycles

(a) Recovery of Au(III) in the presence of an excess of Cu(II)[a]

Cycle	1	2	3	4	5
Adsorbed/mg	1.87	1.84	1.95	1.93	1.82
Eluted/mg	1.73	1.74	1.77	1.75	1.69
Recovery (%)	92.5	94.5	91	91	93

[a] Feed concentration of metal ions: Au(III)/Cu(II) = 20/100 mg l^{-1}, feed time = 15 h. The sorption of Cu(II) was negligible.

(b) Competitive sorption of Pd(II) and Pt(IV)[b]

	Pd(II)			Pt(IV)		
Cycle	Adsorbed/mg	Eluted/mg	Recovery (%)	Adsorbed/mg	Eluted/mg	Recovery (%)
1	4.89	4.16	85	3.79	3.45	91
2	2.64	2.27	86	4.44	3.75	84.5
3	3.59	2.98	83	5.33	4.63	87
4	2.74	2.34	85.5	4.51	4.03	89

[b] Feed concentration of metal ions: Pt(IV)/Pd(II) = 20/20 mg l^{-1} (cycle 1), Pt(IV)/Pd(II) = 100/20 mg l^{-1} (cycle 2–4), feed time = 24 h.

following cycles, the concentration of Pt(IV) was increased to 100 mg l^{-1}. The results as shown in Table 2 are highly significant as not only does the sorption of the two metals take place competitively but also the recovery percentage lies between 80–90% for both of the metal ions.

Conclusion

The PAB-paper gel, prepared by simple chemical modification of waste paper, exhibited remarkable capacity and efficiency for the preconcentration and separation of gold, platinum and palladium from other co-existing metal ions at low to high concentration levels. The high sorption capacity for gold is very interesting because Au(III) is reduced by the gel, after sorption, to the elemental form and gold aggregates are formed. In contrast, Pt(IV) and Pd(II) are sorbed only by pure ionic interaction and their oxidation states remain unchanged. The fact that valuable high demand metals can be recovered by using waste paper looks promising for its practical future application. From an economic viewpoint, this gel raises the prospect for recovering expensive metals at low cost and, from the environmental viewpoint, this gel is quite environmentally benign and acceptable.

Experimental

Materials

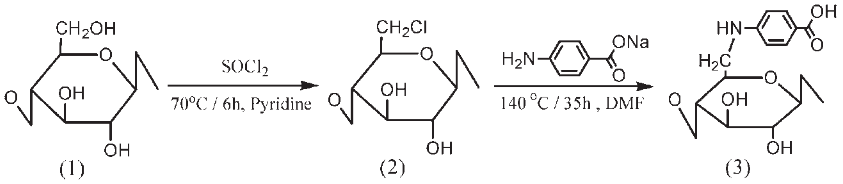
Waste newspaper was used as the feed material for the sorption gel. Thionyl chloride was purchased from Sigma Aldrich, USA and sodium *p*-aminobenzoate from Tokyo Chemical Industries (TCI), Japan. Analytical grade chloroauric acid and chloroplatinic acid (both from WAKO, Japan) were used to prepare the Au(III) and Pt(IV) test solutions, respectively. Ion exchange resins *viz*. Diaion WA 30, Diaion WA21 and Diaion CR11 were acquired from the Mitsubishi Chemical Corporation, Japan. All other chemicals used for the synthesis and for the sorption tests were of analytical grade and were used without further purification.

Methodology

The amount of sorption was calculated from the difference in metal concentration before and after sorption and the weight of the sorption gel. Metal ion concentrations were measured by using a Shimadzu model ICPS-8100 ICP/AES spectrometer. The IR spectra of the sorption gel were measured with a JASCO model FTIR-410 using KBr pellets. A Shimadzu model XRD-610D (LabX) series X-ray diffractometer was used to record X-ray diffraction spectra (XRD) using a 2θ range of 10–80° and a scanning rate of 1° min^{-1}. Scanning electron microscopy (SEM) analysis of the sorbent was carried out using a Hitachi model E1030 Ion Sputter and Hitachi model S-3000, 132-10, EDAX scanning electron microscope under an acceleration voltage of 15 kV (magnification = 100×). An Orion triode electrode, ORION 900011 model (Thermo Electron Corporation) was used for measurement of the oxidation reduction potential (ORP) using a platinum electrode and an Ag/AgCl reference electrode filling solution.

Preparation of the sorbent

For the preparation of the *p*-aminobenzoic acid modified paper gel, waste newsprint paper was treated with sodium hydroxide and washed several times with water in order to remove any soluble impurities. Chemical modification was performed according to Scheme 1. First, 5 ml of thionyl chloride was dropped onto 0.5 g of pre-treated paper (**1**), immersed in 25 ml of pyridine for about 1 h in a N_2 atmosphere and ice-bath conditions. After 1 h, the reaction mixture was heated for 6 h in an oil bath at 70 °C. The resultant compound was mixed with water and filtered. It was washed with water many times till neutral pH and then dried in an oven for a day at 50 °C. This intermediate product *i.e.* chlorinated paper (**2**), was immersed in 25 ml of DMF and 1 g of sodium *p*-aminobenzoate, dissolved in a minimum amount of water, was added. The reaction mixture was stirred with heating at 130 °C in an oil-bath for 35 h. The resulting solid was filtered, treated with 0.1 M HCl, washed with water till neutral pH and then dried for a day at 60 °C. This *p*-aminobenzoic acid modified paper gel (**3**) (0.43 g, 86%



Scheme 1 Preparation of the PAB-type waste paper gel.

yield), which is called hereafter PAB-paper gel, was characterised by IR spectra and elemental analysis.

Sorption tests

A preliminary kinetic study of the uptake for Au(III), Pd(II) and Pt(IV) ions using the PAB-paper gel was carried out to determine the optimum time needed to reach equilibrium. The uptake behaviour of the PAB-paper gel for Au(III), Pd(II), Pt(IV), Cu(II), Fe(III), Ni(II) and Zn(II) was individually examined at varying hydrochloric acid concentrations (0.1 to 4 M). For each metal ion, the initial metal concentration was 0.2 mM. 15 ml of the test solution were mixed together with 20 mg of the gel in stoppered flasks and shaken for 24 h using a thermostated shaker maintained at 30 °C. Similar batch tests were carried out for the uptake of Au(III), Pd(II) and Pt(IV) on unmodified waste paper for comparison.

Sorption isotherms of Au(III), Pd(II) and Pt(IV) on the PAB-paper gel were also obtained by using test solutions of varying concentrations of these metal ions, *i.e.* 0.5–10 mM in 1 M hydrochloric acid solution. Fifteen ml of each of the test solutions were mixed together with 20 mg of the sorption gel and shaken for 60 h at 30 °C.

Column experiment: sorption and elution

Because of the co-existence of precious metals together with other metal ions in a number of practical applications, a flow experiment for the separation of low concentrations of Au(III) from a high concentration of Cu(II) was carried out. A column packed with 0.1 g of the PAB-paper gel was prepared. Prior to passing the test solution, the column was conditioned with distilled water followed by 1 M hydrochloric acid solution for 24 h. Meanwhile, a test solution containing about 20 mg l^{-1} of Au(III) and 100 mg l^{-1} Cu(II) was prepared in 1 M hydrochloric acid. This solution was then pumped at a constant flow rate of 6.5 ml h^{-1} through the column using an Iwaki model PST-100N peristaltic pump. The output solution was collected at 1 h time intervals using a Bio-Rad model 2110 fraction collector prior to the measurement of metal concentrations.

To elute the sorbed metal ions, the loaded column was first washed with water and then with a mixture of 0.15 M thiourea and 1 M hydrochloric acid at a flow rate of 6.5 ml h^{-1}. The output solution was collected similarly at 30 minute time intervals prior to the measurement of the metal concentration. Similarly, for sorption-elution cycle tests, the column was loaded by passing the test solution containing 20 mg l^{-1} Au(III) and 100 mg l^{-1} Cu(II) in 1 M hydrochloric acid for 15 h and the sorbed metal ion (Au only) was eluted by the same method as described above. The sorption/elution operation was repeated five times. The cycle test for Pd(II) and Pt(IV), (both 20 mg l^{-1} in 1 M hydrochloric acid, passing time = 24 h) was also carried out four times under similar conditions.

ORP study

For the ORP measurement, a stock solution containing 2mM Au(III) in 1 M HCl was prepared. Fifteen ml of the solution was mixed together with 20 mg of the gel in sample bottles and shaken in a thermostated shaker at 30 °C for varying time intervals after which the ORP was measured. The residual concentration of Au(III) ion was measured after filtration, as described above.

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