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Recovery of Gold from Hydrochloric Acid by using Lemon Peel Gel

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Abstract: Recovery of Au(III) in aqueous hydrochloric acid medium using lemon peel was studied. The adsorption gel prepared from lemon peel was found to adsorb Au(III) highly selectively showing negligible affinity for other precious metals and some base metal ions studied so far. The adsorption isotherm study gives the maximum loading capacity of the gel as 6.5 mol per kg dry weight of gel. XRD analysis and the digital micrograph of the gel taken after adsorption reveal the formation of gold particles during the adsorption process which is associated with the high selectivity and capacity of the gel for Au(III). Kinetic and electrochemical studies were performed at various temperatures. An endothermic adsorption process following pseudo-first order kinetics was established.

Keywords: Gold adsorption, lemon peel, precipitation

INTRODUCTION

Research trends in the area of metal separation, removal, and recovery are gradually focusing on sorption-active materials prepared from biomass wastes, as biomasses exhibit special metal-binding properties associated with their unique molecular orientation. Although some chemical treatment is needed to change the physico-chemical structures of biomass to make them more active and effective for metal binding, use of biomass is beneficial from both environmental and economic aspects. Orange and apple juice residue, chitosan, sea weeds, and saw

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dust are typical examples of biomasses found to be effective in adsorbing heavy metal ions (1–5). Similarly, some chemically modified biomass wastes like wood lignin, natural or persimmon tannin, chitin, etc. have shown high prospective in precious metals recovery, especially in gold (6,7). From our previous study it has been established that polyphenol-rich materials like crosslinked lignophenol gels and persimmon peel gel have high selectivity for Au(III) (8–11). Hence, it is expected that other biomass wastes with similar natural compositions can be effective in gold recovery. In this context, similar to wood lignin and tannins, the peels of citrus fruits also contain phenol-group-rich components, which means waste citrus fruit peels may also be useful in gold recovery (12).

One third part of citrus fruits is processed to obtain several products, mainly juice (13). The amount of residue obtained from juicing accounts for 50% of the original amount of whole fruit The residue is mainly constituted peel or rind, which is almost one-fourth of the whole fruit mass remaining after juice and essential oil extraction (14), and it is mainly used to obtain pectin and as animal feed. The use of juicing byproducts is needed to reduce costs and to provide a correct solution for the pollution problem connected with the process. Lemon (Citrus × limon) is cultivated primarily for its juice, though the pulp and rind (peel) are also used for some cooking purposes (15). Its peel is rich in different types of polyphenols like limocitrin, limocitrol, luteolin, diosmetin, apigenin, quercetin, etc. made by the binding of hydroxyl, mithoxy, and cellulose units on flavonoid body. Similar to other citrus fruits, lemon residue generated after the extraction of juice or essential oil is also being wasted. To date, any effective application of the waste lemon peel in the field of metal recovery has not been defined.

With an ever increasing application for widely diverse purposes, gold is always in high demand. Despite the need for gold, gold used in the circuit board of various e-appliances, as for example, is being dumped at the end of the life of appliances. It is known that in comparison to copper and some other metals, the mass of gold in e-appliances is negligible. However, the expected mass of gold in e-waste is more than in its natural ore. Hence, considering the harsh effect linked with excessive mining and loss of valuable metals in the form of e-wastes, attention should be given to the recovery of gold from city-mines or e-wastes.

Besides cyanide treatment, aqua regia and chlorine-hydrochloric acid treatment are the commonly used methods of gold leaching. Due to poor selectivity, the mechanical breakdown of the beads and the requirement for complex elution and regeneration process (16) commercially available resins are not good options for the recovery of gold from a mixture of several ions in such strongly acidic chloride medium. Large improvements have been achieved in the last few years through the development of several chelating resins (17–19). Instead, natural materials or biomass wastes from certain industries with a high capacity for precious metals can be obtained with little cost.

Similar to the infrastructure of lignin or tannin in persimmon peel, biomolecules in lemon peel are mostly polyphenols which implies that the residue of lemon juicing can also be used for the purpose of metals recovery. In the present study, the prospective application of lemon peel for gold recovery from hydrochloric acid medium is explained.

EXPERIMENTAL

Materials Used

Analytical grade chloride salts of copper, iron, palladium, tin, and zinc were used to prepare test solutions of respective metals. Analytical-grade $HAuCl_4.4H_2O$ and $H_2PtCl_6.6H_2O$ were used to prepare gold and platinum solutions, respectively. Analytical-grade ascorbic acid, oxalic acid, and gallic acid were used to prepare solutions of required concentration. [CAS –purity etc.]

Determination of Concentration of Polyphenol in Lemon Peel

The approximate quantity of polyphenols contained in lemon peel was measured by the Folin-Denis method. Folin-Denis reagent was prepared by dissolving 10 g sodium tungstate dihydrate ($NaWO_4.2H_2O$), 2.0 g phosphomolybdic acid, and 5.0 ml phosphoric acid in 70 ml distilled water, and heated at 110°C for 2 h. After cooling, the volume of the above solution was set at 100 mL by diluting with water and used as a Folin-Denis reagent. Sodium carbonate was dissolved in 5 mL distilled water, and its supernatant was used as a saturated sodium carbonate solution. About 1 g lemon peel was crushed and mixed with 4 ml of 80% methanol using a homogenizer. The mixture was centrifuged for 10 min at 2000 rpm, and the supernatant liquid was collected. Same process was repeatedly done for 6 times, and the supernatant liquid of each time was collected in the same flask and was referred to as sample 1. A mixture of 10.2 ml sample 1, 3.2 ml distilled water, 0.2 ml Folin-Denis reagent, and 0.4 ml saturated sodium carbonate was incubated for 30 min at ambient temperature to obtain the final test solution. The concentration of polyphenol in the solution was measured by using a UV-Visible spectrometer at 700 nm. For the evaluation of total polyphenols, calibration curves were drawn using a standard solution of various polyphenols like catechin, catechol, pyrogallol, gallic acid, and tannic acid.

Preparation of Lemon Peel Gel

For the preparation of lemon peel gel, sulfuric acid was used as a crosslinking medium. Raw lemon peel was collected and crushed into fine pieces by using a Dalton model P-3S power mill. An adequate amount of crushed lemon peel was mixed with concentrated sulfuric acid, and the mixture was stirred for 24 h at 100°C in order to enhance the condensation reaction for crosslinking. The product was filtered, neutralized with sodium bicarbonate solution, washed several times with distilled water, dried in a convection oven for 24 h, and finally crushed to get powder. The dried rigid mass of crosslinked lemon peel gel is referred to as lemon gel hereafter in this paper.

Adsorption Tests

Adsorption behavior of the lemon gel was first tested batchwise. Solutions with 0.2 mM of individual metals were prepared in varying concentration of hydrochloric acid. 10 mL of the metal solution was mixed with 10 mg of the gel and shaken for 24 h at 30°C to attain the equilibrium. The percent adsorption for each metal ion was calculated according to Equation (1), where C_i is the initial concentration of metal ion and C_e stands for the equilibrium concentration measured after adsorption on lemon gel.

$$\%\ Adsorption = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

Kinetics of the adsorption of Au(III) on lemon gel were studied at various temperatures (10°C–50°C) by taking 10 mL of 2 mM Au(III) solution prepared in 0.1 M HCl together with 10 mg lemon gel. In order to examine the oxidation-reduction property of lemon gel, the redox potential of the Au(III)–lemon gel was measured at different time intervals at 30°C. An adsorption isotherm study for Au(III) was performed by varying the initial concentration of Au(III) solution in 0.1 M hydrochloric acid medium.

Measurement Methodology

Metal concentrations before and after adsorption were measured by using Shimadzu model AA-6650 atomic absorption spectrophotometer. The initial and equilibrium concentration of hydrochloric acid was measured by titration with sodium hydroxide solution using phenolphthalein indicator. The X-ray diffraction spectra were recorded using a Rigaku type RINT-8829 X-ray diffractometer. A KEYENCE model VHX/VH series micro photographer was used to take the digital micrographs. An Orion model 9180BN triode ORP electrode was used for the *emf* measurement.

RESULTS AND DISCUSSION

Polyphenols Content in Lemon Peel

Approximate concentrations of polyphenols in lemon peel were measured according to the Folin-Denis method. As tannic acid, gallic acid, pyrogallol, catechol and catechin were used as typical standards for this measurement, as shown in Fig. 1, the polyphenol content varies with the nature of standard used in the calibration. The highest concentrations were calculated from the catechin standard. Although the exact cause of this difference is not clear, this figure suggests there is a high concentration of pyrogallol type group. In addition, the measurement has given the evidence of substantial quantities of polyphenols in the lemon peel.

Effect of Crosslinking

From Fig. 1 it is clear that polyphenols are abundant in lemon peel. For this reason, significant adsorption of gold by the peel without crosslinking is

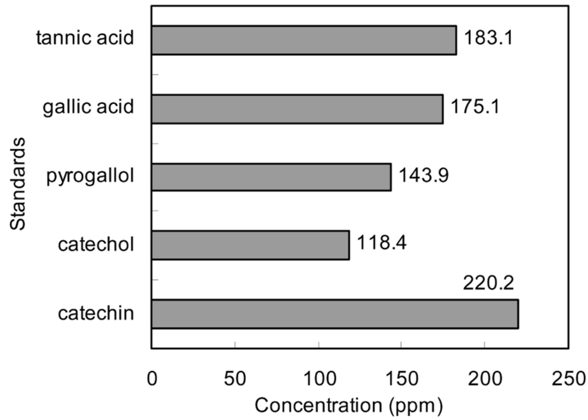

Figure 1. Approximate amount of polyphenol is lemon peel based on various standards.

expected. The kinetics of reduction of gold were studied by mixing 20 mg uncrosslinked lemon peel and 10 ml 0.5 mM Au(III) in 0.1 M hydrochloric acid. Similar tests were done by taking 10 mg lemon gel and 10 ml of 1.8 mM Au(III) in 0.1 M hydrochloric acid As shown in Fig. 2, faster and higher reduction of Au(III) was observed for 10 mg gel whereas it is slow and not significant in the case of 20 mg peel. This result suggests the necessity of crosslinking of the lemon peel to improve its physico-chemical properties which activates the material enhancing its Au(III) loading and subsequent reducing ability.

Adsorption Kinetics and ORP Study

The adsorption kinetics of Au(III) on lemon gel were studied at various temperatures: 10, 30, 40, and 50°C. Figure 3 shows the % adsorption of Au(III) and the ORP change during the adsorption process. At 10°C, the adsorption is very slow, and the ORP change is also not noticeable. At 30°C, more than 50% adsorption was observed at 24 h, and it became nearly 100% at 40 and 50°C The ORP change was noticeable at 40°C, and a sharp decrease was observed at 50°C. With the increase in temperature, faster kinetics were observed suggesting that the adsorption of Au(III) on lemon gel is an endothermic process, and faster recovery can be achieved by increasing the temperature (Figures 3, 4).

Based on the kinetic study at different temperatures, the order of adsorption of Au(III) on lemon gel was analyzed. From the slopes of

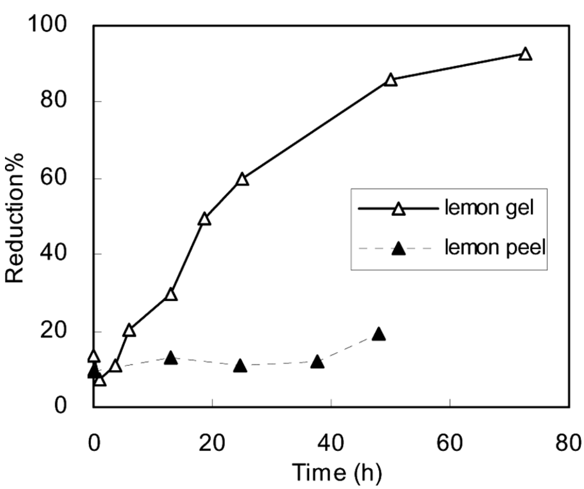

Figure 2. Effect of crosslinking on the loading capacity of lemon gel.

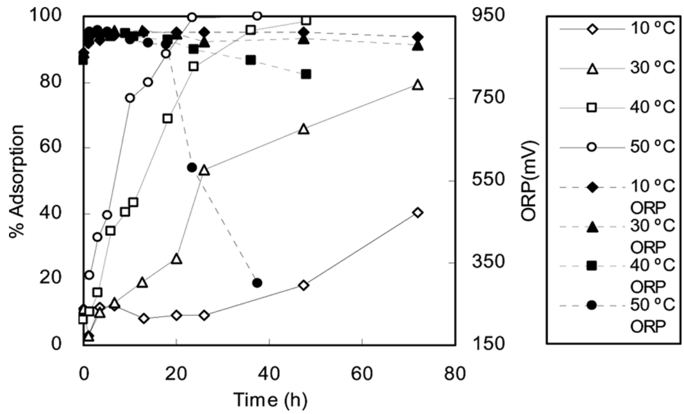

Figure 3. Kinetics of Au(III) adsorption on lemon gel at various temperatures and variation of ORP.

the plots of ln(Ce/Ci) as a function of time, the rate constants for 10, 30, 40, and 50°C were calculated as 0.0061, 0.0223, 0.0791, and 0.1857 h^{-1}, respectively. From the relationship between rate constant and temperature, the Arrhenius plot as shown in Fig. 4b was obtained from which the activation energy, E_a, was calculated to be 64.8 kJ/mol The result indicates that the adsorption and subsequent reduction of Au(III) on lemon gel follows the pseudo-first order adsorption kinetics and is endothermic.

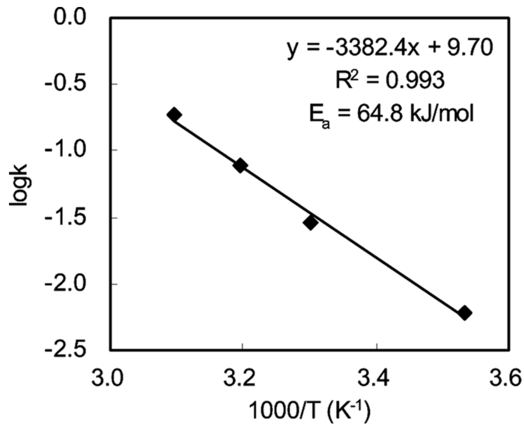

Figure 4. The Arrhenius plot for the adsorption of Au(III) on lemon gel.

For the evaluation of various thermodynamic parameters of the adsorption of Au(III) on lemon gel, following well established relationships can be applied.

$$\Delta H = E_0 - RT \tag{2}$$

$$\Delta G = \Delta H - T\Delta S \tag{3}$$

where T is the reaction temperature, ΔH is the enthalpy of adsorption, E_a is the energy of activation, R is the universal gas constant, ΔG is the Gibbs free energy change, and ΔS is the entropy change. In order to evaluate the values of all thermodynamic parameters from the activation energy and the rate constant the Van't Hoff equation (Eqs. 4 and 5) is applicable.

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{4}$$

$$\Delta G = -RT \ln K \tag{5}$$

Using the relationship in Eq. 2, the enthalpy of adsorption was calculated. Also, Eq. 5 gives the free energy and the entropy can be obtained from Eq. 3. All the parameters evaluated from these equations are given in Table 1. The negative values of the Gibbs free energy change (ΔG) indicate that the adsorption process is favorable. The positive enthalpy (ΔH) reveals energy is absorbed as adsorption proceeds, and the reaction is endothermic, which results in the equilibrium extent of reaction increasing with increasing temperature. The entropy changes in this study are found to be positive; it means that the increased randomness appeared on the gel–solution interface during the adsorption of Au(III). The positive entropy change may be due to the release of water molecule produced by adsorption process.

Table 1. Kinetic and thermodynamic parameters evaluated for the adsorption of Au(III) on lemon gel at different temperatures

Temperature (K)	[HCl] mol/dm^3	R^2	First order rate constant (s^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
283	0.1	0.801	1.70×10^{-6}	62.44	−25.85	311.99
303	0.1	0.971	6.19×10^{-6}	62.28	−24.40	286.10
313	0.1	0.982	2.20×10^{-5}	62.20	−21.91	268.74
323	0.1	0.951	5.16×10^{-5}	62.11	−20.32	255.24

Adsorption Behavior of Metal Ions on Lemon Gel

Figure 5 shows the percent adsorption of Au(III), Cu(II), Fe(III), Pd(II), Pt(IV), Sn(IV), and Zn(II) on lemon gel at varying hydrochloric acid concentration. Highest selectivity was observed for Au(III) whereas the gel was found to exhibit only weak extractability for other metal ions. The percent adsorption of Au(III) was nearly independent of hydrochloric acid concentration. Although some extractability was observed for Pt(IV), it was much lower in comparison to Au(III). From this result it is obvious that the lemon gel has very high selectivity for Au(III) and is expected to adsorb Au(III) preferentially from a number of precious or base metals tested so far. Selectivity tests were also performed using binary mixtures of Au(III)-Cu(II) and Au(III)-Sn(IV) under the same experimental condition. From these tests lemon gel was also found to adsorb Au(III) with negligible affinity for Cu(II) or Sn(IV).

Adsorption Isotherm of Au(III) on Lemon Gel

As the lemon gel was found to be selective only for Au(III), test of adsorption isotherm was carried out for Au(III) ion. Figure 6 shows the adsorption isotherm of Au(III) at HCl concentration of 0.1 M. From this figure, it is clear that the adsorption increases with increasing gold concentration in low concentrations and approaches a constant value at around 6.5 mol/kg dry gel or about 1.3 kg gold per kg dry weight of gel.

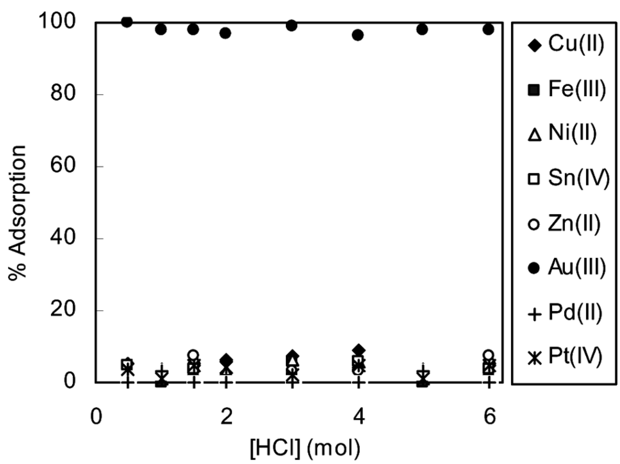

Figure 5. Adsorption behavior of lemon gel for various metal ions. Initial metal concentration = 0.2 mmol, temperature –303 K, contact time –24 h.

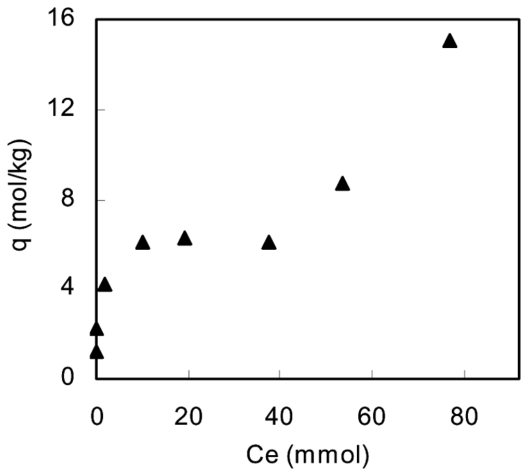

Figure 6. Adsorption isotherm of Au(III) on lemon gel. Gel weight = 10 mg, solution volume = 10 ml, temperature = 303 K, contact time = 50 h.

After reaching a plateau, the curve again increases with further increase in concentration of Au(III) in higher concentration region. In the low concentration region, adsorption took place according to the Langmuir monolayer adsorption model, and at higher concentrations BET multilayer adsorption appears to occur. According to this model, the energy of the second adsorption layer formation is lower than that of the first and hence, it is inferred that, after the formation of the first layer, the formation of the second layer starts with ease. This result is very interesting due to the occurrence of multilayer adsorption which is not a common phenomenon in typical chemical adsorption. In addition, the above mentioned result shows the feasibility of selective uptake of Au(III) from low to high concentration by using lemon gel. In this context it is important to note that the feedstock of lemon gel is the lemon peel, which is usually treated only as a waste. After a simple chemical modification this otherwise useless material can be used to recover gold with excellent selectively and very high loading capacity.

CONCLUSION

Lemon peel waste could be highly effective in recovering Au(III) from aqueous hydrochloric acid medium after simple chemical modification. Its excellent selectivity and very high loading capacity make it a high prospective substrate for Au(III) recovery from a mixture of several metal ions. As the adsorption was found to be followed by reduction to elemental form, gold recovered using lemon peel is expected to be free of foreign elements. According to the kinetic and electrochemical study, both the adsorption and reduction processes are endothermic showing faster adsorption rates and an *emf* drop with a small elevation of temperature. Use of this kind of biomass waste, which costs virtually nothing, for recovering valuable metal like gold would be an inspiring breakthrough, especially in the metal recycling from e-wastes.

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