Adsorption of Gold (III) from Aqueous Solutions on Bagasse Ash

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Summary: To assess the potential of cheap biomass materials for the recovery of gold from industrial, and electroplating waste water effluents, adsorption of gold (III) from dilute solutions of hydrochloric acid on bagasse ash has been studied under various experimental conditions by using batch technique. Percentage extraction of gold (III) on bagasse ash was determined from its distribution coefficients as a function of contact time, pH, adsorbent, adsorbate concentrations, and temperature. The uptake of gold (III) by bagasse ash is time, pH, metal concentration, amount of adsorbate, and temperature dependent. Adsorption data have been interpreted in terms of Langmuir, and the Freundlich equations. Thermodynamic parameters for the adsorption of gold (III) on bagasse ash have been determined at three different temperatures. The positive value of heat of adsorption; ΔH^o = 44.52 kJ/mol shows that the adsorption of gold (III) on bagasse ash is endothermic where as the negative value of ΔG^o = -0.5303 kJ/mol at 318 K shows the spontaneity of the process. ΔG^o becomes more negative with increase in temperature which shows that the adsorption is more favorable at higher temperatures. Under the optimal adsorption conditions the adsorption capacity of gold is 0.70 mg /g of the adsorbent out of which 0.65 mg of gold gets desorbed with 0.1 % thiourea solution.

Introduction

Precious metals including gold have been historically important as currency, and although still remain as investment commodities but because of their specific physical, and chemical properties are now widely used in industry, agriculture, and medicine. Gold, and colloidal gold have been extensively studied as therapeutic agents, and it has been shown that nanoparticles of gold possess novel catalytic, optical, magnetic, and electronic properties, and as labels for X-ray crystallography, and electron microscopy [1].

Most of the conventional technology for the recovery of gold from ores involves the use of chemical methods such as cyanidation, and thiourea leaching which presents environmental, and health risks [2-4]. For a very long time gold was being separated on commercial basis from the aqua regia leach solutions of the metal concentrates by precipitation with iron(II) sulphate subsequent to its refining by electrolytic methods; iron(II) sulphate precipitation gave problems with the effluents, and the process of electrolysis was time-consuming. Later on a selective solvent extraction method was developed in 1968 by Morris, and Khan [5] which is even now being used on commercial basis for the separation, and refining of gold from aqua regia leach solution of the electrolytic mud obtained from the electrolytic refining of nickel, and copper, and any other precious metal concentrates. Though some of the solvent extraction procedures are very selective but these methods because of high cost, and low feasibility have their limited applications when used for solutions containing low concentration of gold [6]. The conventional methods for the removal of metal ions from secondary sources such as waste water effluents include oxidation, reduction, precipitation, membrane filtration, ion-exchange, and adsorption. Among all these methods adsorption is highly effective, and economical [7, 8]. Activated carbon has been used for adsorption of gold as $[AuCN]^{-2}$ complex from the cyanide leach solutions, and some ion-exchange resins have also been used for the recovery of gold from aqueous solutions [9], but separation of adsorbed metal from the adsorbent, and the ion exchange resins becomes quite difficult, and some times achieved only by burning the resin which leaves tar, coke, and waste materials.

The demand of gold because of its vast industrial applications is increasing day by day, and because of its high price these days, there is a need to develop a cheap, and environmental friendly method for the recovery of gold from secondary sources such as electronic scrap, jewellery workshop wastes, industrial, and electroplating waste water effluents. Much interest has been developed in the recent years in the use of non conventional materials such as microbacteria i.e. bacteria, peat, algae, fungi, and various other biosorbents for the separation of heavy toxic metals as well as precious metals from waste water effluents [10-12]. Various biosorbents materials such as alfalfa (Medicago Sativa) biomass has been used for the adsorption studies of gold (III)

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from the solutions of hydrochloric acid as $[AuCl4]^{-1}$ [13]; where as waste crab shells have been used for the adsorption of gold from cyanide solutions as $[AuCN]^{-2}$ [14]. Adsorption of gold from aqueous solutions onto L-lysine modified cross linked chitosan resin has also been recently studied [7]. Adsorption of gold-thiourea complex has also been studied on bagasse ash [15-19]. Very recently orange peel, sawdust, and bagasse ash have been used for the adsorption of various metal cations from aqueous solutions [20, 21]. The mechanism of adsorption of metal ions to biomass materials is believed to occur at cell walls via ion exchange, complexation, electrostatic binding, and / or precipitation [22].

Results, and Discussion

Effect of Shaking Time

The adsorption of gold (III) on bagasse ash was studied as a function of shaking time at 35°C. 10 cm^3 of 5.07×10^{-6} M gold (III) solution was shaken with 0.2 g of bagasse ash for different intervals of time ranging from 10 min to 50 min in a thermostatted water shaker bath at 35 ± 0.5 °C. Fig. 1 shows the variation of percentage adsorption, P, with shaking time. These results show that the adsorption process is rapid, and time dependent. At first the extent of adsorption increases with an increase in shaking time. Percentage adsorption, P, attains almost a maximum value after 20 minutes after which there is no significant change occurs up to 50 minutes. Very rapid adsorption in the beginning shows that the adsorption of gold on bagasse ash may be due to electrostatic binding of gold with some functional groups in the bagasse ash or exchange of the metal with some ions on the surface of the adsorbent. Thirty minutes shaking time was used for all other experiments.
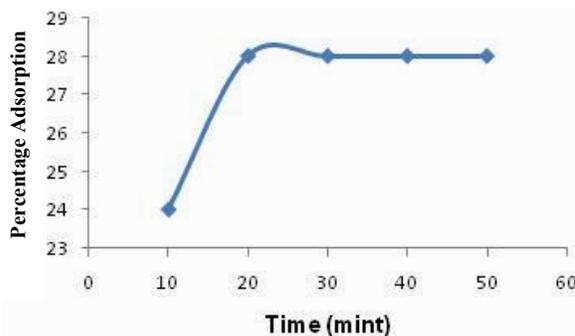
Fig. 1:   Variation in percentage adsorption of gold (III) as function of shaking time.

Effect of pH

The effect of pH on the adsorption of gold (III) on bagasse ash from 5.07×10^{-6} M gold solution was studied at 35 ± 0.5 °C by varying the pH of the solution from 1 to 10. Fig. 2 shows the variation of percentage adsorption, P, with pH. These results show that the percentage adsorption initially increases gradually with increasing pH which gets to a maximum value at pH 4, afterwards percentage adsorption decreases with increasing pH. It has been shown that biomass materials containing amine as functional groups would adsorb metal anionic ions from aqueous solutions due to electrostatic attraction. Functional groups containing amines will dominantly be positively charged in acidic media due to protonation which will promote the adsorption of negatively charged $[AuCl4]^{-1}$ ions by strong electrostatic interaction.
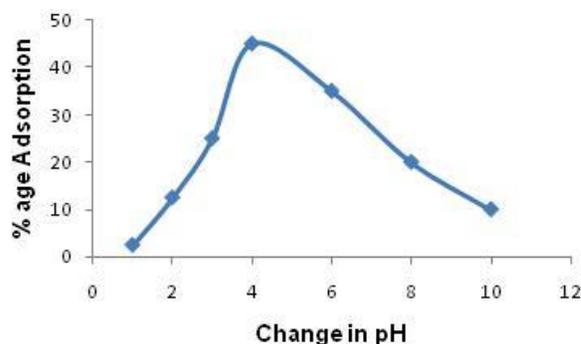
Fig. 2:   Variation in percentage adsorption of gold (III) as function of different pH.

$$R\text{-}NH_2 + H^+Cl^- \rightarrow RNH_3^+Cl^-$$
$$2RNH_3^+Cl^- + AuCl_4^- \rightarrow (RNH_3^+)_2AuCl_4^- + 2Cl^-$$
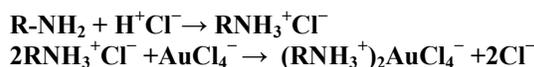
As the pH increases beyond 4 the amine functional groups are gradually deprotonated, and the surface density will drastically decrease with increasing pH leading to the decrease in the attractive electrostatic interaction between the adsorbent, and the gold complex. Our results are in good agreement with the previously reported gold adsorption studies from hydrochloric, and cyanide solutions on various biomass materials [22-25]. The maximum adsorption occurs at pH 4 therefore all other experiments were carried out at this pH.

Effect of Adsorbent Concentration

The dependence of gold (III) adsorption from 5.07×10^{-6} M solution on the amount of bagasse

ash was studied by varying the amount of adsorbent from 0.2 to 1.0 g/10 cm³ of the solution while keeping all other parameters constant at 35±0.5 °C. The results are shown in Fig. 3. The percentage adsorption of gold (III) on bagasse ash increases almost gradually with the increasing amount of the adsorbent. The increase in the percentage adsorption with increasing amount of the adsorbent is because of the greater availability of the exchangeable/ adsorption sites at higher concentration of the adsorbent.
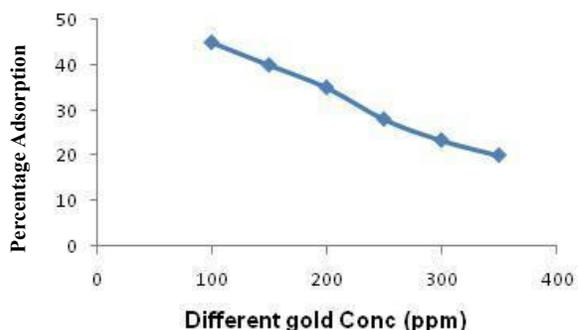
Fig. 3: Variation in percentage adsorption of gold (III) as a function of different amount of adsorbent.

Effect of Adsorbate Concentration

The adsorption of gold (III) on bagasse ash as a function of its concentration was studied at 35±0.5 °C by varying the metal concentration from 5.07×10^{-6} M to 1.17×10^{-5} M, while keeping all other parameters constant. The results are shown in Fig. 4. The percentage adsorption of gold (III) on bagasse ash gradually decreases with increasing the bulk metal concentration in the aqueous solution. These results also indicate that at lower metal concentration the greater adsorption is due to the greater availability of the functional groups on the adsorption sites, as the metal concentration increases, the decrease in the adsorption is due to the lesser availability of the functional groups carrying positive charge.

Adsorption Isotherms

The adsorption isotherms of gold (III) on bagasse ash were studied at three different temperatures i.e. 308K, 313K, 318K by varying the metal bulk concentration in the solution from 5.07×10^{-6} M to 1.17×10^{-5} M, while keeping all other parameters constants. Fig. 5. shows the plot of gold (III) adsorbed on bagasse ash (g/g) against metal

concentration in the solution at equilibrium, Ce. These isotherms show that the amount of gold (III) adsorbed per unit weight of bagasse ash increases with an increase in temperature. The adsorption results have been analyzed in terms of Freundlich, and Langmuir adsorption isotherms.
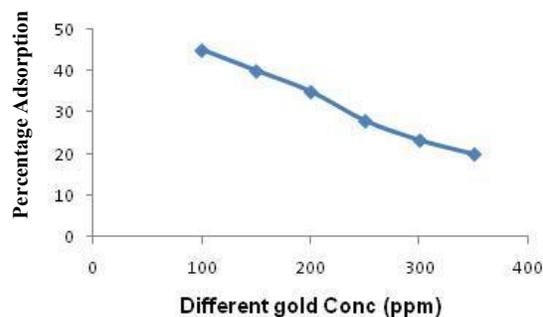
Fig. 4: Variation in percentage adsorption of gold (III) as a function of different conc. of gold.
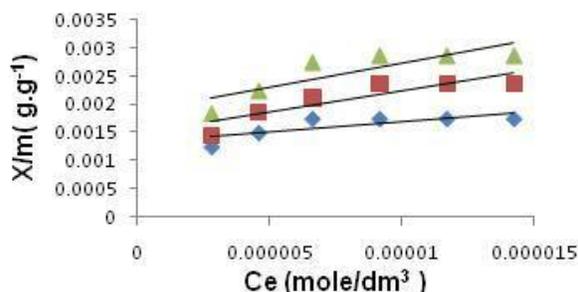
Fig. 5: Adsorption isotherms of gold (III) on bagasse ash at three different temperatures: 308 K(◆); 313 K (■); 318 K (▲).

Freundlich Isotherms

The data obtained for the adsorption of gold (III) on bagasse ash in the equilibrium concentration, Ce, ranging from 2.79×10^{-6} to 11.92×10^{-6} mol/dm³ were fitted to the Freundlich equation. The following linearized form of the Freundlich equation was used.

log X/m = log K + 1/n log Ce   (1)

where X/m is the amount adsorbed per gram of the adsorbent, Ce is the equilibrium concentration of gold in the solution, K, and 1/n are the empirical constants which are characteristic of the system, and depend on nature of the adsorbent, nature of the adsorbate, temperature, and pressure. The plot of log X/m against log Ce for gold (III) adsorption on bagasse ash gives a straight line with positive slope 1/n, and intercept log K. This is shown in Fig. 6. The

values of the constants 1/n, and log K were obtained from the slope, and the intercept of the plot, respectively. Linear regression of the plot gave a slope less than 1, indicating a concentration dependent adsorption of gold (III) on bagasse ash in the concentration range studied. The values of Freundlich constants K, and n which are related to adsorption capacity, and intensity respectively are given in Table-1.
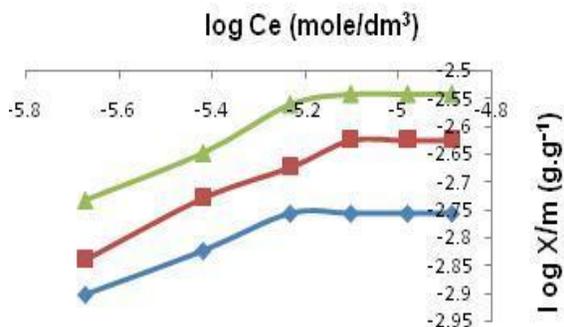
Fig. 6:   Freundlich isotherms of gold (III) adsorption on bagasse ash at three different temperatures:
308 K(◆); 313 K (■); 318 K (▲).

Table-1: Values of Freundlich constants for gold (III) adsorption on bagasse ash.

Temperature (K)	Slope (1/n)	Intercept (logK)	N	K (mg/g)	R^2
308	0.204	-1.7379	4.9019	0.0182	0.827
313	0.280	-1.2230	3.5714	0.0598	0.917
318	0.212	-1.4660	4.71069	0.0341	0.886

Langmuir Isotherms

Following linearized form of the Langrnuir's equation was used for analyzing the adsorption data for the adsorption of gold (III) on bagasse ash:

$$\frac{Ce}{X/m} = \frac{1}{Q_m} Ce + \frac{1}{Q_m . K_L} \qquad (2)$$

where X/m is the amount of gold adsorbed per unit mass of the adsorbent. Ce is the equilibrium concentration of the metal in the solution. Q_m is the saturation amount of the metal per unit amount of the adsorbent or which is generally called the monolayer capacity, K_L is the binding constant which is determined from the linear plots of Ce/x/m Vs Ce as shown in Fig. 7.

The plot of Ce/(x/m) Vs equilibrium concentration Ce in Fig. 7 shows conformity of the gold adsorption data with equation (2). The values of Q_m i.e. the mono layer capacity for adsorption, and the binding constant K_L have been calculated from the from the slopes, and intercepts of the plots respectively. These values are given in Table-2.
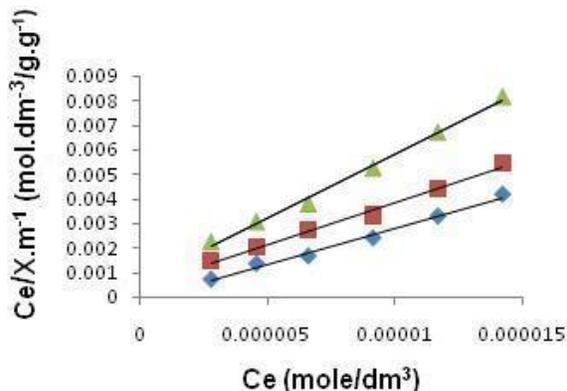
Fig. 7:   Langmuir isotherms of gold (III) adsorption on bagasse ash at three different temperatures:
308 K(◆); 313 K (■); 318 K (▲).

Table-2: Values of Langmuir constants for gold (III) adsorption on bagasse ash.

Temperature (K)	Slope (1/Q_m)	Intercept (1/Q_m.K_L)	Q_m (mol/g)	K_L (dm³/mg)	R^2
308	518.38	0.000612	1.9290×10^{-03}	3.1521	0.994
313	365.14	0.000622	2.7386×10^{-03}	4.4030	0.995
318	320.09	0.000278	3.1241×10^{-03}	11.237	0.996

Thermodynamic Parameters for the Adsorption System

Thermodynamic parameters for the adsorption of gold (III) on bagasse ash such as heat of adsorption, ΔH^o (enthalpy change), entropy change, ΔS^o, and free energy of specific adsorption, ΔG^o were calculated from the binding constant Kc obtained from the Langmuir plot by using the following equations [20, 26-28].

$$\ln K_c = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (3)$$

$$\Delta G^o_C = -RT \ln K_c \qquad (4)$$

$$K_c = \frac{C}{Ce} \qquad (5)$$

where R is the gas constant, Kc is the equilibrium constant, T is the temperature (K), C is the equilibrium concentration of Au(III) on adsorbent (mg/L), and Ce is the equilibrium concentration of Au(III) in the solution (mg/L).

The heat of adsorption, $\Delta H°$, and entropy change, $\Delta S°$, for gold (III) adsorption on bagasse ash was calculated from the slope, and intercept of the Van't Hoff linear plot of log Kc versus 1/T as shown in Fig. 8. The free energy of adsorption, $\Delta G°$, for gold (III) adsorption on bagasse ash was calculated by using the following equation:

$$\Delta G° = - RT \ln Kc \qquad (6)$$
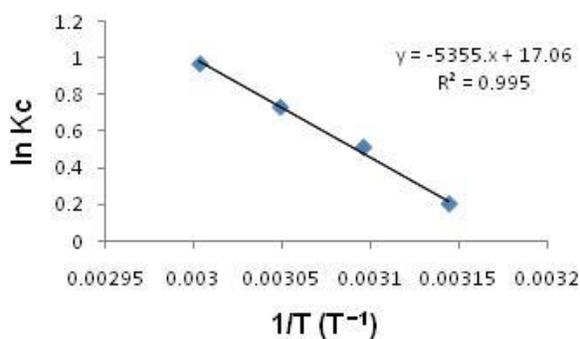
Fig. 8: The plot of In Kc vs 1/T for gold (III) adsorption on bagasse ash.

The values of thermodynamic parameters $\Delta H°$, $\Delta S°$, and $\Delta G°$ for gold (III) adsorption on bagasse ash were calculated by using equations 3 to 6, are given in Table-3.

Table-3: Values of thermodynamic parameters for gold (III) adsorption on bagasse ash.

Slope ($-\Delta H°/R$)	Intercept ($\Delta S°/R$)	$\Delta H°$ (KJ/mol)	ΔS (KJ.Mol^{-1}.K^{-1})	$\Delta G°$ (KJ/mol)			
				318K	323K	328K	333K
-5355.85	17.06	44.52	0.1418	-0.5303	-1.3714	-1.9228	-2.6835

The plots in Fig. 5 and 7, and increase in the value of Kc at higher temperatures show the endothermic character of gold adsorption on bagasse ash. $\Delta H°$ for gold adsorption on bagasse ash is 44.52 kJ/mol. The negative values of the free energy of specific adsorption $\Delta G°$, for the adsorption of gold (III) on bagasse ash, Table-3, indicate the spontaneity of the process. The value of $\Delta G°$ becomes more, and more negative as the temperature increases, indicating more driving force, and hence resulting in greater adsorption capacity at higher temperatures.

The increase in the adsorption capacity of gold (III) on bagasse ash at higher temperature may be attributed to the enlargement of the pore size or activation of the adsorbent surface. The greater extent of gold adsorption at higher temperatures becomes quite apparent by an increase in the monolayer capacity. The results in Table-2 show that the monolayer capacity Q_m for gold adsorption on bagasse ash is 1.92 m mol /100g of the adsorbent at 308K which increases to 3.12 m mol /100g of the adsorbent at 318K.

The adsorption of gold on bagasse ash is an endothermic process; it can only occur spontaneously if the entropy of the system increases, and the value of T$\Delta S°$ becomes more than the value of $\Delta H°$ so as to give negative value of the free energy of specific adsorption, $\Delta G°$. The adsorption of gold on bagasse ash is accompanied by an increase in the entropy of the overall system. The positive value of $\Delta S°$ shows increase in the randomness at the solid/solution interface during the adsorption of the metal ion on the bagasse ash. Our results are in good agreement with the results of some other base metal ions adsorption on bagasse [20].

Desorption of the Adsorbed Metal

Under the optimal adsorption conditions the adsorption capacity of gold is 0.70 mg / g of the **a**dsorbent out of which 0.65 mg of gold gets desorbed with 0.1 % thiourea solution 4.

Experimental

Adsorbent

Bagasse, the fibrous by-product of sugarcane milling operation, was collected from ashraf sugar mills Bahawalpur in large quantities which was initially dried in direct sunlight for three days, and then was placed in an oven at 60 °C for twenty four hours. Dried bagasse was thoroughly washed with distilled water to remove any dirt, and foreign materials, and was again dried in an oven at 100ºC for about two hours. Then the dried bagasse was crushed, ground, and sieved through a 30-mesh screen. The ground material was again washed with distilled water to remove any adhering dirt, and foreign particles. It was then kept in an oven at 60 °C for 24 hours. The bagasse ash was obtained by heating the covered material in an oven at 160 ºC for 2 hours which was then ground, and was sieved through a 350-mesh screen.

Gold Stock Solution

5.07 × 10^{-3} M gold stock solution was prepared by dissolving 0.25g of pure gold metal strip into 60 cm^3 of *aqua regia* over a steam bath in a covered beaker. Once the metal was dissolved, HNO_3 was fumed off by adding conc. HCl, and this was again heated near to dryness, this was repeated three times, and finally solution was transferred into 500 ml measuring flask, and volume was made up to the mark with distilled water. Various other gold solutions of different concentrations were made by taking known aliquots of the stock solution, and then diluting it to the known calculated volume.

Preparation of TMK Solution

0.06% TMK, 4,4-bis(dimethylamino)-thiobenzophenone, (Thio-Michler's Reagent) solution was prepared by dissolving 15 mg of the reagent in 25 cm^3 of ethanol with continuous mixing. This solution being very light sensitive, therefore was kept in a dark bottle rapped in an aluminum foil, and was kept in the refrigerator. This solution under these conditions remains stable for one month.

Preparation of Surfactant

5% Triton X-100 solution was prepared by dissolving 5ml pure Triton X-100 into 100 cm^3 of distilled water with slow heating over burner. Once surfactant was dissolved in distilled H_2O, it was made up to 100 cm^3 with distilled water.

General Procedure

The general method used for the adsorption of gold on bagasse ash is described below:

0.1 g or in some cases 0.4g of the dried sieved bagasse ash was equilibrated with 10 cm^3 of the gold solution of known concentration in a stoppered Pyrex glass flasks at a fixed temperature in a thermostated shaker water bath for a known period of time. The flasks containing the weighed amounts of bagasse ash, and gold solution were separately kept in the thermostated bath before mixing for a sufficient period of time to attain the desired experimental temperature. After equilibration the suspension was centrifuged in a stoppered tube for 20 minutes at 3500 rpm. The concentration of gold in a known volume of the supernatant was determined spectrophotometerically by using Double Beam Spectrophotometer (Laborned, UVD-3500) by using TMK reagent, triton-X 100 surfactant, and a buffer

solution of pH 3.5 [29-31]. The amount of gold adsorbed on the bagasse ash was thus determined in terms of percentage adsorption P% which was calculated from the distribution coefficient Kd. The amount adsorbed per unit mass of adsorbent, x/m was also calculated.. These are described below.

The distribution coefficient Kd, is defined as the concentration of a species adsorbed per gram of the adsorbent divided by its concentration per cm^3 in the liquid phase:

$$K_d = \frac{m_s/M}{m_e/V} \; Cm^3/g$$

where m_s, and m_e are the masses of the metal adsorbed, and in solution respectively, M is the mass of the adsorbent in gram, and V is the volume of the solution in cm^3.

The percentage adsorption, P, was calculated from Kd by using the following equation:

$$P = \frac{100 \times Kd}{Kd + V/m} \; \%$$

Amount adsorbed per unit weight of the bagasse ash, x/m, was calculated from the initial known metal concentration, and final amount of the metal in the solution after equilibrium.

Conclusions

The results of this study indicate that fibrous by-product of sugarcane waste such as bagasse ash could very effectively be used for the recovery of gold from industrial, and electroplating waste water effluents containing low concentrations of the metal. Maximum adsorption of gold from hydrochloric acid solutions occurs by adjusting the pH of the aqueous solution to 4; adsorbed metal could easily be desorbed with 0.1 M thiourea solution. This method has been successfully used to recover gold from some samples of waste water effluents from a commercially operating gold electroplating unit in the city of Wah, Pakistan.

References

1. M. A. Hayat, Ed. Colloidal Gold. Principles, Methods and Applications, Academic, San Diego (1989).
2. G. Deschenes, *Journal of Hydrometellurgy*, **20**, 180 (1998).

3. G. Gamez, J. L. Gardea-Torresdey, K. J. Tiemann, J. Parsons, K. Dokken and M. J. Yacaman, *Journal of Advances in Environmental Reasearch*, **7**, 563 (2003).

4. A. Hafeez, U. Ali and M. A. Khan, *Journal of the Chemical Society of Pakistan*, **32**, 753 (2010).

5. D. F. C. Morris and M. Ali Khan, *Talanta*, **15**, 301 (1968).

6. M. A. Khan, Proceedings of the International Symposium on Applications and Technology of ionizing Radiations, **3**, 1453 (1982).

7. K. Fujiwara, A. Ramesh, T. Maki, H. Hasegawa and K. Ueda, *Journal of Hazardous Materials*, **146**, 39 (2007).

8. N. Gonen, E. Korpe, M. E. Yıldırım and U. Selengil, *Journal of Minerial Engineering*, **20**, 559 (2007).

9. M. Soleimani and T. Kaghazchi, *Jornal of Bioresource Technology*, **99**, 5374 (2008).

10. D. E. Salt, R. C. Prince, A. J. M. Baker, I. Raskin and I. J. Pickering, *Journal of Environmental Science Technology*, **33**, 713 (1999).

11. J. P. Young and J. F. Derek, *Journal of Hazardous Materials*, **164**, 1152 (2009).

12. S. Syed, *Journal of Hydrometallurgy*, **82**, 48 (2006).

13. J. L. Gardea-Torresdey, K. J. Tiemann, G. Gamez, K. Dokken and N. E. Pingitore, *Journal of Advances in Environmental Research*, **3**, 83 (1999).

14. H. Niu and B. Volesky, *Journal of Hydrometallurgy*, **71**, 209 (2003).

15. N. Syna and M. Valix , *Journal of Mineral Engineering*, **16**, 511 (2003).

16. M. J. Iqbal and M. N. Ashiq, *Journal of the Chemical Society of Pakistan*, **32**, 419 (2010).

17. Noor-ul-Amin, *Journal of the Chemical Society of Pakistan*, **32**, 481 (2010).

18. Noor-ul-Amin, K. Ali and M. T. Shah, *Journal of the Chemical Society of Pakistan*, **31**, 357 (2009).

19. Noor-ul-Amin, K. Ali and M. T. Shah, *Journal of the Chemical Society of Pakistan*, **31**, 370 (2009).

20. K. Ali, Noor-ul-Amin and M. T. Shah, *Journal of the Chemical Society of Pakistan*, **31**, 375 (2009).

21. M. Ajmal, R. A. Khan Rao, R. Ahmad and J. Ahmad, *Journal of Hazardous Materials*, **79**, 117 (2000).

22. A. Habib, N. Islam, A. Islam and A. A. M. Shafiqul, *Pakistan Journal of Analytical and Environmental Chemistry*, **8**, 21 (2007).

23. B. Volesky and, Z. R. Holan, *Journal of Biotechnology Progress*, **11**, 235 **(**1995).

24. Z. Tao, F. Xiaoyi, M. Tao, W. Jian and L. Zhongfan, *Langmuir*, **15**, 5197 (1999).

25. T. Tsuruta, *Jornal of Genenral and Applied Microbiology*, **50**, **221** (2004).

26. J. L. Gardea-Torresdey, K. J. Tiemann, G. Gamez, K. Dokken and M. J. Yacaman, Proceedings of the Conference on Hazardous waste research, pp. 122-130 (1998).

27. S. A. Khan and M. A. Khan, *Journal of Radioanalytical and Nuclear Chemistry Articles*, **190**, 81 (1995).

28. S. A. Khan, *Journal of Radioanalytical and Nuclear Chemistry*, **258**, 3 (2003).

29. Y. Liu, *Journal of Chemical and Engineering Data*, **54**, 1981 (2009).

30. A. J. Christopher, *Analyst*, **94**, 397 (1969).

31. X. S. Zhang, C. S. Lin, G. J. Quiao and L. Z. Liu, *Journal of Chromatography*, **39**, 693 (1994).