

Recovery of Gold from Electroplating Waste Water Effluents by using Orange Peel

ASIM HAFEEZ, USMAN ALI AND MUHAMMAD ALI KHAN*
Institute of Chemistry, University of the Punjab, New Campus Lahore Pakistan.

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Summary: A method for the recovery of gold from the electroplating waste water effluents has been developed based on its adsorption on orange peel. Adsorption of gold(III) from dilute solutions of hydrochloric acid on orange peel has been studied under various experimental conditions by using batch technique. Distribution coefficients, K_d and % extraction were determined for the orange peel-gold solution system as a function of contact time, pH, sorbent, sorbate concentration, sorbate dose, and temperature. The uptake of gold by raw orange peel is time, pH, initial metal concentration, sorbate dose, and temperature dependent. Adsorption data have been interpreted in terms of Langmuir and the Freundlich equations. Thermodynamic parameters for adsorption of gold on raw orange peel have been determined at three different temperatures. The positive value of heat of adsorption; $\Delta H^\circ = 61.85$ kJ/mol shows that the adsorption of gold on orange peel is endothermic whereas the negative value of $\Delta G^\circ = -35.85$ kJ/mol at 308 K shows the spontaneity of the process. ΔG° 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 5.79 mg/g of the raw orange peel out of which 5.37 mg of gold gets desorbed with 0.1 % thiourea solution.

Introduction

Most of the conventional methods for the extraction of gold from ores involve the use of chemical methods such as amalgamation, cyanidation and thiourea leaching which present environmental and health risks [1-6]. For a very long time gold was being separated on commercial basis from the aqua regia leach solutions by precipitation with iron(II) sulphate subsequent to its refining by electrolytic methods [7], iron(II) sulphate precipitation gave problems with the effluents and the process of electrolysis was time-consuming. Latter on a selective solvent extraction method was being developed in 1968 by Morris and Khan which is now even being used on commercial basis for the separation and refining of gold from the aqua regia leach solutions of the electrolytic mud obtained from the electrolytic refining of copper and nickel [8]. Some other methods such as adsorption of gold on activated carbon as $[\text{AuCN}]^{-2}$ complex from the cyanide leach solutions and ion-exchange resins have also been used for the recovery of gold from aqueous solutions [9, 10], 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. Though some of the solvent extraction procedures are very selective but these methods have their limited applications because of high cost and low feasibility when used for solutions containing low concentrations of gold [11].

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 environmentally friendly method for the recovery of gold from secondary sources such as electronic scraps, 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 peat, algae, and various biosorbents for the separation of heavy toxic metals as well as precious metals from waste water effluents [12]. Various biosorbent materials such as alfalfa has been used for the adsorption of gold(III) as $[\text{AuCl}_4]^{-1}$ from the solutions of hydrochloric acid [13] where as waste crab shells have been used for the adsorption of gold from cyanide solutions as $[\text{AuCN}]^{-2}$ [14]. Very recently orange peel wastes have been used for the adsorption studies of various base metal cations from aqueous solutions [15, 16]. 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 [17].

Citrus fruit is very abundantly available in Pakistan and its peel which is thrown away as a waste could prove to be a good adsorbent for some metal ions from aqueous solutions. Adsorption and desorption of gold has therefore been studied on

*To whom all correspondence should be addressed.

dried and sieved orange peel under various experimental conditions to establish the optimal conditions for its maximum recovery from aqueous solutions containing low concentrations of the metal. The adsorption data have been interpreted in terms of Freundlich and Langmuir equations and various thermodynamic parameters have also been determined.

Results and Discussion

Effect of Shaking Time

The adsorption of gold on orange peel was studied as a function of shaking time at 25 ± 0.5 °C at pH 4. 10 cm^3 of $7.1 \times 10^{-6} \text{ mol dm}^{-3}$ gold solution was equilibrated with 0.5 g of orange peel for different intervals of time ranging from 10 minutes to 50 minutes in a thermostated shaker water bath at 25 ± 0.5 °C. Fig.1 shows the variation of distribution coefficient, K_d , and percentage adsorption, %, with shaking time. These results show that adsorption of gold(III) on orange peel is time dependent. At first the extent of sorption increases with an increase in shaking time. Both K_d and % adsorption attain almost maximum values after 20 minutes and do not change appreciably later on up to 50 minutes. Very rapid adsorption in the beginning shows that the sorption of gold on orange peel may be due to electrostatic binding of gold with some functional groups in the orange peel. Thirty minutes shaking time was selected for all further studies.

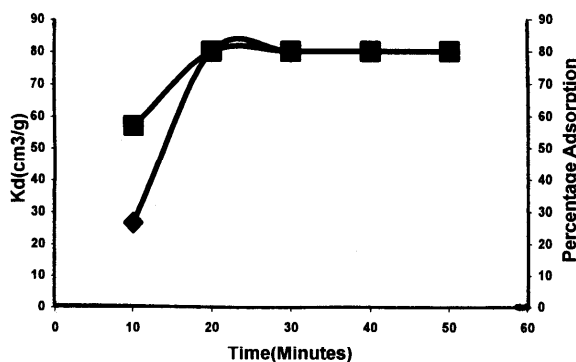


Fig. 1: Effect of shaking time on the sorption of gold from $7.1 \times 10^{-6} \text{ mol dm}^{-3}$ solution on 0.5 g orange peel. K_d (◆); Percentage adsorption (■).

Acid treated orange peel was found to have lower adsorption capacity for Au(III) from dilute solutions of hydrochloric acid than the raw orange peel, therefore all the other experiments were carried out on the raw orange peel.

Effect of pH

The effect of pH on adsorption of $5.07 \times 10^{-6} \text{ mol dm}^{-3}$ gold solution on 0.1 g of orange peel was studied at 25 ± 0.5 °C by varying the pH of the supernatant solution of gold solution and the adsorbent from 1.4 to 11 at solution to solid ratio of 100:1. The results in Fig.2 show that the adsorption of Au(III) on orange peel increases with increasing pH. Both K_d and percent adsorption increase with an increase in pH up to pH 4 where adsorption attains a maximum value, thereafter adsorption decreases as the pH increases. The Adsorption of Au(III) was found to be closely related to the pH of the solution. It has been shown that biomass materials containing amine as functional groups would adsorb metal anionic ions from aqueous solutions due to electrostatic attraction [18]. Functional groups containing amines will dominantly be positively charged in acidic media due to protonation which will promote the adsorption of negatively charged $[\text{AuCl}_4]^{-1}$ ion by strong electrostatic interaction. 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

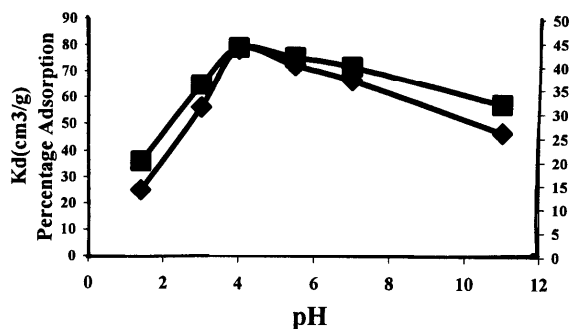


Fig. 2: Effect of pH on the sorption of gold from $5.07 \times 10^{-6} \text{ mol dm}^{-3}$ solution on 0.1 g orange peel. K_d (◆); percentage adsorption (■).

hydrochloric and cyanide solutions on various biomass materials containing amine as the functional groups [19-21]. The maximum adsorption of gold(III) from dilute hydrochloric acid solutions occurs at pH 4 therefore all other experiments were carried out at this pH.

Effect of Adsorbent Concentration

The dependence of gold adsorption on the amount of raw orange peel was studied by varying the amount of the adsorbent from 0.1 to 0.4 g /10 cm³ of 6.091×10⁻⁶ mol dm⁻³ gold solution at 25 ± 0.5 °C while keeping all other parameters constant. The results are shown in Fig.3. Both K_d as well as the percent adsorption increase almost gradually with the increasing amount of the adsorbent. The increase in the % adsorption and K_d values of Au(III) with the increasing amount of the orange peel is due to the availability of the more adsorption sites with greater amount of the adsorbent.

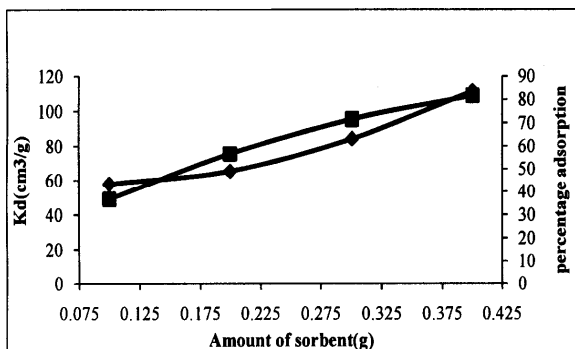


Fig. 3: The dependence of gold adsorption on the amount of orange peel for 6.091×10⁻⁶ mol dm⁻³ gold solution. K_d (♦); Percentage adsorption (■).

Effect of Sorbate Concentration

The effect of gold concentration on its adsorption on orange peel was studied at 25 ± 0.5 °C by varying the metal concentration from 6.09×10⁻⁶ to 1.218×10⁻⁵ mol/dm³ while keeping all other parameters constant. Fig.4 shows the variation in the % adsorption and K_d values of gold(III) adsorption on orange peel against the gold bulk concentration in the solution. Both % adsorption and K_d values gradually decrease as the metal concentration increases. These results indicate that at lower metal concentration the greater adsorption is due to greater availability of the functional groups on the adsorption sites.

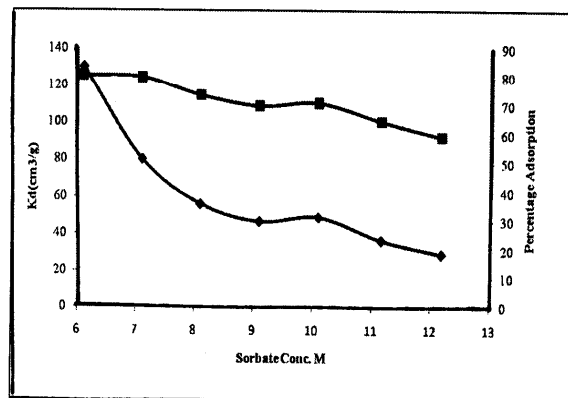


Fig. 4 Effect of gold concentration on its sorption on orange peel at 25 ± 0.5 °C, Distribution coefficient, K_d(♦) and percentage adsorption (■).

Adsorption Isotherms

The adsorption isotherms for gold adsorption on raw orange peel were obtained at three different temperatures by varying the gold bulk concentration in the solution from 6.09×10⁻⁶ to 1.015×10⁻⁵ mol/dm³, while keeping all other adsorption conditions constant, *i.e.* solution to solid ratio 20:1, pH 4 and shaking time 30 minutes. Fig 5 shows the plots of gold adsorbed on orange peel against metal concentration in the solution at equilibrium, C_e. The results are analyzed in terms of Freundlich and Langmuir isotherms.

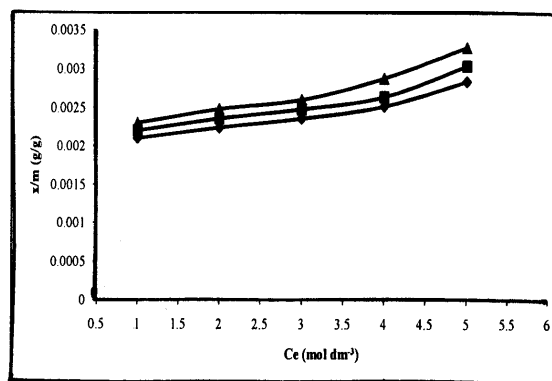


Fig. 5: Adsorption isotherms of gold on orange peel at different temperatures: 298 K (♦); 303 K (■); 308 K (▲)

Data obtained for the adsorption of gold in the concentration range 6.09 x 10⁻⁶ to 1.015 x 10⁻⁵

mol/dm³ were fitted to Freundlich isotherm [22]. The following linearized Freundlich equation (1) was used;

$$\text{Log} \frac{X}{m} = \text{Log} K_f + \frac{1}{n} \text{log} C_e \quad (1)$$

where X/m is the amount of gold adsorbed per unit mass of the adsorbent, C_e is the equilibrium concentration of gold in the solution; $1/n$ and K_f are constants dependent on the temperature. A plot of $\text{log} X/m$ against $\text{log} C_e$ gives a straight line, the slope and intercept of which correspond to $1/n$ and $\text{log} K_f$, respectively. Freundlich plot for gold adsorption on orange peel for metal concentration in the solution at equilibrium ranging between 6.09×10^{-6} to 1.01×10^{-5} mol/dm³ is shown in Fig.6. Linear regression of the plot gave slope of less than 1, indicating a concentration dependent adsorption of gold in the concentration range used. The value of Freundlich exponent $1/n$ is 0.14.

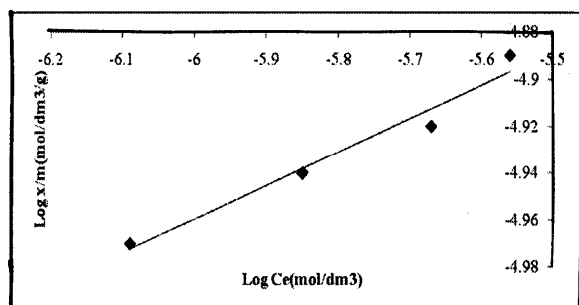


Fig. 6: Freundlich plot of gold adsorption on orange peel at 298 K (◆).

The following well known form of the Langmuir equation (2) has been used [23].

$$\frac{C_e}{X/m} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_m} \quad (2)$$

where x/m is the amount of gold adsorbed per unit weight of orange peel, C_e is the metal concentration in the equilibrium solution, Q_m is the saturation

amount of adsorbate per unit amount of the adsorbent or which is generally called the monolayer capacity, and K is a constant related to the intensity of adsorption. A Langmuir plot showing conformity of the adsorption data with equation (2) for gold concentration in the solution at equilibrium ranging between 7.106×10^{-6} to 9.137×10^{-6} mol/dm³ at three different temperatures *i.e.* 298 K, 303 K, 308 K are shown in Fig. 7. The values of Q_m *i.e.* the monolayer capacity for adsorption and the binding constant K were calculated from the values of the linear plots of $C_e/X/m$ Vs C_e , from the slopes and intercepts respectively, these values are given in Table-1.

The heat of adsorption, ΔH° , was calculated from Langmuir's constant K_1 also called Binding constant, determined from the linear plots of $C_e/X/m$ Vs C_e , Fig. 7. The ratio of slope/intercept gives the value of K , which is related to the heat of adsorption by the following equation:

$$K = K_0 e^{-\Delta H/RT} \quad (3)$$

Equation (3) in the logarithmic form is written as:

$$\text{In} K_c = \frac{-\Delta H^\circ}{RT} + \text{Constant} \quad (4)$$

And

$$\text{In} K_c = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (5)$$

A plot of $\text{In} K$ Vs $1/T$ shown in Fig 8 gives a straight line; the value of ΔH is calculated from the slope of the line. The value of ΔH for adsorption of gold on orange peel at saturation is given in Table-2.

Thermodynamic Parameters

Thermodynamic parameters were determined by employing the following equations which have earlier been used by us and others [15, 24-28].

Free energy of specific adsorption, ΔG° , was calculated from the following equation:

Table-1: Values of the langmuir constants for gold adsorption on orange peel.

Temperature (K)	Slope= (1/Q _m)	Intercept (1/Q _m .K ₁)	Q _m (Monolayer - Capacity) (mol/g)	Q _m (mg/g)	K ₁ (b) (Binding Const.)	R ²
298	4.4×10 ⁴	0.083	2.272×10 ⁻⁵	4.475	5.30×10 ⁵	0.984
303	4.3×10 ⁴	0.053	2.325×10 ⁻⁵	4.58	8.11×10 ⁵	0.985
308	3.4×10 ⁴	0.028	2.941×10 ⁻⁵	5.79	12.14×10 ⁵	0.918

Table-2: Values of thermodynamic parameters for the sorption of Au(III) on orange peel.

ΔH° (kJ/mol)	ΔS° (kJmol ⁻¹ K ⁻¹)	ΔG° (kJ/mol)		
		298K	303K	308K
61.85	0.3172	-32.65	-34.26	-35.85

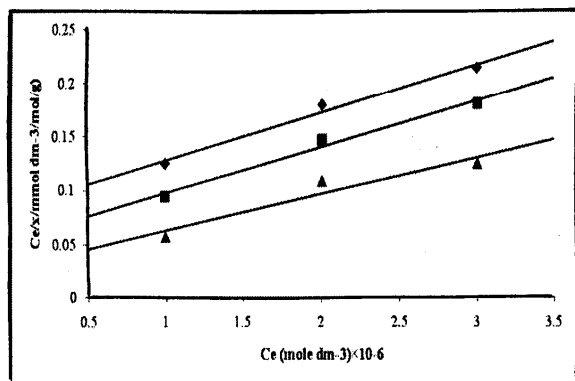


Fig. 7: Langmuir plots of gold sorption on orange peel at different temperatures: 298K (◆); 303 K (■); 308 K (▲).

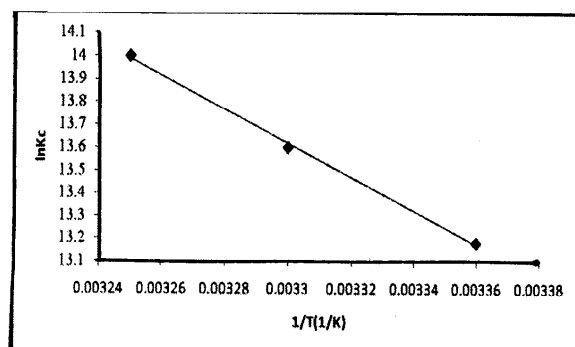


Fig. 8: Plot of lnKc vs 1/T for gold sorption on orange peel.

$$\Delta G^\circ = - RT \ln K_c \quad (6)$$

where K is the binding constant and its value is obtained from the Langmuirs plot, Fig. 8. The entropy change ΔS° for the gold orange peel system was calculated by using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (7)$$

The plots in Fig. 5 and 7 and increase in the value of K_c at higher temperatures show the endothermic character of gold adsorption on orange

peel. ΔH° for gold sorption on orange peel is 61.85 kJ/mol. The negative values of the free energy of specific Adsorption ΔG° , Table-2, show that sorption of gold on orange peel is a spontaneous process. The value of ΔG° becomes more negative as temperature increases indicating that sorption is favored at higher temperatures. The increase in the adsorption capacity of orange peel 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 orange peel is 4.47 mg /g at 298K which increases to 5.79 mg /g at 308 K.

The adsorption of gold on orange peel is an endothermic process; it can only occur spontaneously if the entropy of the system increases and the value of $T\Delta S^\circ$ become more positive than ΔH° so as to give negative value of the free energy of specific adsorption, ΔG° . The adsorption of gold on orange peel is accompanied by an increase in the entropy of the overall system (Table-2). The positive value of ΔS° shows the increase in the randomness at the solid/solution interface during the adsorption of the metal ion on the orange peel. Our results are in good agreement with the results of some other base metal ions adsorption on orange peel [15].

The Presence of Other Metal Ions

The effect of various metal cations like lead, nickel, cobalt barium, iron and sodium on the adsorption of gold(III) on the orange peel has been studied at $25 \pm 0.5^\circ\text{C}$. 5 cm^3 of separate solutions of lead, nickel, cobalt, barium, iron and sodium having concentration of $1.01 \times 10^{-5}\text{ mol/dm}^3$ was separately mixed with 5 cm^3 of $1.01 \times 10^{-5}\text{ mol/dm}^3$ gold solution. This was equilibrated with 0.5 g of orange peel for 30 minutes at $25 \pm 0.5^\circ\text{C}$. In one of the experiments all of the above mentioned metal cations were taken together with the gold solution and were equilibrated with 0.5 g of the adsorbent to check the overall effect. The distribution ratio (K_d) and % adsorption were determined by usual method. The values of K_d and % adsorption do not change appreciably in the presence of these metal cations. Therefore these metal cations do not interfere in the adsorption of gold on orange peel. The non interference of these metal cations with gold adsorption is quite obvious

because the adsorption of these metal cations would occur on different type of the functional groups other than amines.

Desorption Studies

Under the optimum adsorption conditions, 1.42 mg of gold from 10 cm³ of dilute hydrochloric acid solution containing 2.0 mg of the metal gets adsorbed on 0.5 gram of the orange peel and 1.34 mg of the adsorbed metal gets desorbed with 10 cm³ of 0.1 mol dm⁻³ thiourea: HCl (1:1) solution. These results indicate that under the optimal experimental conditions the adsorption capacity of gold is 5.79 mg/g of the adsorbent out of which 5.37 mg (*i.e.* 93%) of gold gets desorbed with 0.1 % thiourea solution.

Experimental

Adsorbent Collection and Preparation

Orange peel was collected from a nearby fruit shop in large quantities and dried in the direct sunlight for three days this was then put in an oven at 45 °C for twenty four hours. Dried orange peel was then crushed ground and sieved through 350 mesh screen. This was then washed with distilled water to remove any adhering dirt and foreign particles. It was again dried in an oven at 45 °C for 24 h.

Acid Treated Orange Peel

50 g of the dried, crushed, ground and sieved raw orange peel was mixed with 200 cm³ of 0.01 mol dm⁻³ HCl for about an hour it was then filtered, washed with distilled water and dried in an oven at 45 °C for 24 h.

Gold Stock Solution

5.07 × 10⁻³ mol dm⁻³ (1000 ppm) gold stock solution was prepared by dissolving 0.1 g of pure gold metal strip into 60 cm³ of aqua regia over a steam bath in a covered beaker, once the metal was dissolved it was further heated to reduce the volume to near dryness, few cm³ of conc. HCl was then added and this was again heated near to dryness to fume off HNO₃, this was repeated three times and finally the volume was made up to 100 cm³ with distilled water. Various other gold solutions of different concentrations were made by taking known aliquots of the stock solution and then making it to the known volume with the distilled water.

Complexing Reagent

0.06 % 4,4'-Bis(dimethylamino)thiobenzophenone (Thio Michler's Ketone, TMK) solution was prepared by dissolving 15 mg of reagent grade TMK from Aldrich Germany into 25 cm³ of ethanol with continuous mixing. This solution was freshly prepared for each experiment.

Surfactant

5 % Triton X-100 solution was prepared by dissolving 5 cm³ of Triton X-100 from Sigma Aldrich Iceberg into 50 cm³ of distilled water with slow heating and then the volume was made up to 10 cm³ with distilled water.

Adsorption Procedure

The adsorption of gold on orange peel was studied by a batch technique. The general method used for these studies is described below.

0.5 g or in some cases 0.1 g of the dried sieved orange peel was equilibrated with 10 cm³ of the gold solution of the known concentration in a stopper 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 the orange peel and the 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 solution was determined spectrophotometrically by using TMK reagent [29-31] and double beam spectrophotometer of Labomed, UVD-3500 and double beam spectrophotometer of Labomed, UVD-3500. The amount of gold adsorbed on the orange peel was thus determined. Adsorption of gold on orange peel was determined in terms of distribution coefficient, K_d, percentage adsorption, % and amount adsorbed per unit mass of the adsorbent, X/m, these are described below:

The distribution coefficient, K_d, is defined as the concentration of the metal adsorbed per gram of the adsorbent divided by its concentration per cm³ in the liquid phase:

$$K_d = \frac{m_s/M}{m_e/V} \text{ cm}^3/\text{g}$$

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, %, was calculated from K_d by using the following equation:

$$\text{Percentage adsorption} = \frac{100 \times K_d}{K_d + V/W} \quad (\%)$$

Amount adsorbed per unit weight of the orange peel, X/m , was calculated from the initial known and the final metal concentration of the metal in the supernatant solutions after adsorption.

Conclusion

The results of this study indicate that citrus fruit waste such as raw orange peel 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 mol dm^{-3} 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.

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