ADSORPTION OF GOLD ON ACTIVATED CARBONS PREPARED FROM SOME TANZANIAN CARBONACEOUS AGROWASTES AND BITUMINOUS COAL

J.E.G. Mdoe and L.L. Mkayula

Department of Chemistry, University of Dar es Salaam, P.O. Box 35061, Dar es Salaam, Tanzania

ABSTRACT. A study on the adsorption capacity and kinetics of gold from aqueous solutions onto activated carbons prepared from some agrowastes and bituminous coal has been made. The carbons were characterised by nitrogen physisorption and their mineral impurities evaluated. The carbons obtained were mostly microporous with BET surface area ranging from 200 to 1000 m^2g^{-1}. They also contained some inorganic materials. The gold adsorption capacity on the carbons was affected by the type of carbon, percentage carbon burn-off (%CBO), pretreatment, temperature and ionic composition of the adsorption medium. All source materials, except rice husks, produced carbons with good adsorption capacity. The adsorption was fast in the first hour and decreased gradually as equilibrium was approached. The adsorption data was best described by an equation proposed by Laidera et al.

INTRODUCTION

Activated carbon has been used successfully in the removal of gold from cyanide solution [1]. Adsorption of gold on activated carbon is an old method, but it was introduced in large scale operations in the beginning of 1970s. Since then a lot of studies have been conducted in order to establish the actual physico-chemical properties of the adsorption process [1-3]. The method has proven to be superior than the traditional process of gold recovery through cementation with zinc powder. Development of efficient elution methods, possibility of carbon regeneration, little loss of soluble gold, and less effect of impurities on the process, are some of the advantages of this process. It also has lower operational and capital costs [4].

Activated carbons can be prepared from a variety of carbonaceous materials. However, the surface chemical and adsorptive properties of a given carbon depend on the starting material, the composition of the activation atmosphere, and the time and temperature of activation [5]. In the gold adsorption process, optimum performance requires the activated carbon to have important characteristics, such as high rate of gold extraction, high gold loading capacity and resistance to abrasion [6].

Activated carbons have been prepared and characterised from some Tanzanian agricultural wastes [7]. The behaviour of such carbons in adsorption from the solution phase was, however, not studied. The nature of the surface (type of oxide and imperfections) of activated carbons, for which numerous mechanisms of gold adsorption have been proposed, is not well understood. So it is the authors conviction that a search for the most well-suited carbon for the recovery of gold must be continued.

In the present study, the adsorption capacity and kinetics of gold on activated carbons prepared from cashew nut shells (CNS), coconut shells (CONS), rice husks (RH), black wattle charcoal (BWC) from *Acacia mearnsii*, and bituminous coal (BCO), have been described in relation to the influences of source materials, level of carbon burn-off, composition of adsorption medium, and temperature.

EXPERIMENTAL

Chemicals. The potassium aurocyanide used in this investigation was supplied by Aldrich. All other chemicals used were of AR grade.

Preparation and characterisation of the activated carbons

Preparation. The procedures for the preparation of the activated carbons and measurements of adsorption isotherms were as described before [7]. Only three samples, *viz.*, 1:2 RH, 1:1 RH and 2:1 RH, were prepared by chemical activation. The rest of the carbons were prepared by CO_2 activation.

Determination of percentage ash. The method and procedure recommended by Sutcliffe Speakman Carbons Ltd. [9] was followed.

Determination of metal content. In a typical procedure, 0.50 g of the ash was added to 25 mL of 2 M HCl and the mixture boiled gently for 5 min. The mixture was then filtered through a glass crucible (porosity 4) and washed 3 times with distilled water. The filtrate and washings were put into 250 mL volumetric flask and diluted to the mark with distilled water. The solution obtained was then analyzed for metal content using a Perkin-Elmer model 2380 atomic absorption spectrophotometer (AAS).

Pretreatment of the activated carbons. The treatment was done by using distilled water or dilute HCl. Treatment with distilled water involved thorough washing of the carbon in hot water by successive soaking and decantation, and then drying at 383 K. Treatment with dilute HCl involved simmering of 1.0 g carbon in 50 mL of 1 M HCl for 10 min. This was followed by thorough washing with distilled water and then drying at 383 K.

Gold equilibrium adsorption tests. A mass of 0.04 g of water-/HCl-treated carbon was agitated at 303 K for 24 h with 100 mL of an aurocyanide solution containing 5 to 50 mg gold per litre, with or without additives. The mixtures were placed in 250 mL Erlenmeyer flasks, and were agitated by a GRANT SS40-A2 linear shaker incubator. After the agitation, the content of each flask was filtered through a Whatman No. 40 filter paper, and the filtrate analyzed for gold content using the AAS. Some experiments were conducted at different temperatures ranging from 303 to 330 K.

Adsorption kinetics tests. Water-treated carbon (0.1 g) was contacted with 800 mL of a solution containing known amount of gold in a flow system [1]. The tests were conducted under nitrogen atmosphere at 303 K. The pH values of the adsorption media were maintained at desired values by the addition of NaOH or HCl. The solutions were agitated with a Teflon-protected magnetic stirring bar. Solution samples, usually 4 mL, were taken at regular intervals and analyzed for their gold content by using the AAS.

RESULTS AND DISCUSSION

The prepared activated carbons which had percentage carbon burn-off (%CBO) ranging from 21 to 82%, are shown in Table 1.

Analysis of N_2 adsorption isotherms and adsorption data. The volumetric adsorption data obtained were used to plot adsorption isotherms (Figure 1). The isotherms were type I in the Kiselev's [9] classification, for both the chemically and physically activated carbons [7]. The results indicate that the carbons are mainly microporous. The isotherms have steep rise at low relative pressures and plateau at high relative pressures. The initial portion of the isotherm becomes steeper and rises higher as %CBO increases. This leads to a conclusion that burn-off has produced many more micropores.

Table 1. Summary of the evaluated properties of the prepared activated carbons.

Type of carbon	S_{BET} (m^2g^{-1})	S_{LANG} (m^2g^{-1})	% Ash of carbon	% Ash of raw material	Metal content (mg g^{-1})						
					K	Na	Ca	Mg	Al	Fe	Pb
65% CONS	1031	1413	6.8		-	-	-	-	-	-	-
60% CONS	980	1375	5.8	0.7	4.89	1.33	0.31	0.32	nil	-	nil
45% CONS	911	1286	5.1		4.23	1.27	0.28	0.27	nil	0.18	nil
22% CONS	653	859	4.1		3.81	1.12	0.19	0.12	nil	0.02	nil
76% CNS	196	252	19.9		-	-	-	-	-	-	-
65% CNS	766	1124	18.6		10.2	1.14	1.77	1.06	0.03	0.12	nil
45% CNS	717	1034	11.9	2.7	9.76	1.02	1.46	1.35	0.01	0.11	nil
21% CNS	441	601	9.0		-	-	-	-	-	-	-
72% BWC	745	1105	-		-	-	-	-	-	-	-
60% BWC	722	1025	2.2		5.45	0.19	11.9	0.65	0.07	0.64	nil
50% BWC	677	997	2.1	1.3	-	-	-	-	-	-	-
45% BWC	642	823	1.5		5.35	0.18	8.74	0.72	0.05	0.43	nil
25% BWC	481	668	1.2		-	-	-	-	-	-	-
65% BCO	815	1249	25.6		-	-	-	-	-	-	-
60% BCO	756	1183	24.8		1.98	0.76	9.78	0.43	10.1	1.99	0.04
45% BCO	529	814	22.9	17.5	1.97	0.64	8.28	0.29	9.04	1.93	0.02
38% BCO	501	785	20.7		-	-	-	-	-	-	-
21% BCO	435	559	17.2		1.25	0.42	8.02	0.35	8.03	1.51	0.03
1:2 RH	645	832	35.0		2.10	0.43	1.81	0.66	nil	0.06	nil
1:1 RH	683	943	35.9	28.1	-	-	-	-	-	-	-
2:1 RH	727	994	36.1		3.25	0.85	1.82	0.74	0.003	0.09	nil

"-" means not determined. The % sign given before each abbreviation shows the %CBO of a particular sample.

Table 1 gives also the S_{LANG} values of the prepared activated carbons as ranging from 250 to 1400 m^2g^{-1}. The data indicate that the surface areas increase with increase in %CBO for a given carbon sample. This suggests that increase in %CBO causes a creation of more pores of nearly the same size, leading to an increase in surface area. However, increase in %CBO above 60% did not cause appreciable increase in surface area for the case of bituminous coal-based carbons. Furthermore, the adsorption isotherms for these carbons at the higher %CBO (about 60%) show narrow hysteresis loops, indicative of wider pores [10] as

depicted in Figure 1. Thus, at this level of carbon burn-off there is coalescence of pores instead of creation of many more micropores as observed at lower %CBO. Further increase in %CBO leads to more coalescence of pores and consequently collapse of the lattice structure of the carbon as exemplified by the surface areas of 76% CNS and 82% BCO.
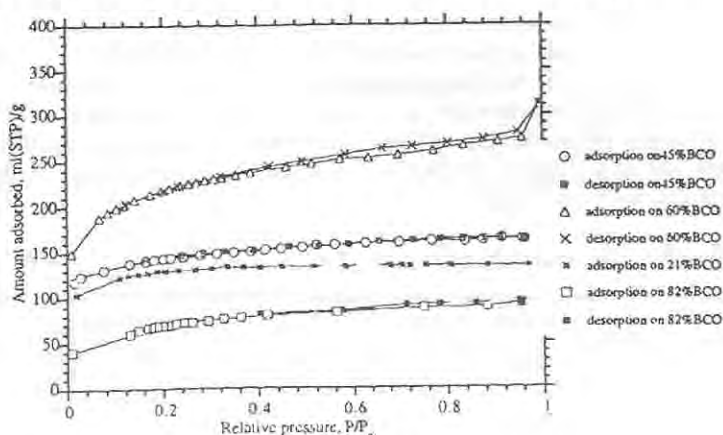

Figure 1. Nitrogen adsorption/desorption isotherms at 77.4 K on BCO carbons.

The S_{BET} and S_{LANG} values increase also with increase in impregnation ratios (amount ratios of KOH to carbon) from, 1:2 to 2:1 for the chemically activated carbons. Since no hysteresis loops are observed, it can be inferred that increase in impregnation ratio causes creation of more micropores.

Mineral impurities found in the activated carbons. Not all impurities found in activated carbons can be volatilized by heat during carbonization and/or activation. Table 1 shows the variation of mineral impurities in the prepared activated carbons quantified as percentage ash and metal content on a w/w basis. Given in the table are also the % ash contents of the starting materials. It was noted that the amount of the impurities varied depending on the type of the starting material and the level of %CBO/impregnation ratio. It was also observed that RH-based carbons had the highest amount of ash, followed by bituminous coal-based carbons. Black wattle-based carbons, on the other hand, had the least amount of ash. Whereas the values for CONS-based carbons are comparable to those obtained by other workers [10], those of black wattle carbons fall below the range obtained by Ahmad *et al.* [11] for carbons prepared from *Acacia arabica*.

The values of the metal content show that BWC carbons have the highest amount of calcium, whereas CNS carbons show the highest amount of potassium and magnesium. Activated carbons prepared from a mineral source (bituminous coal) are the only carbons containing significant amounts of iron and aluminium. They also contain a small amount of lead. The relative metal content thus depends on the type of the source material. It was also observed that, the metal content increased with %CBO. This increase is due to the continual burning of the carbon content as well as expulsion of volatile materials from the carbon, leaving behind the non-volatile materials.

Factors influencing the adsorption of gold on activated carbons.

i) *Effect of carbon type and surface area/percentage carbon burn-off.* Figure 2 shows the gold equilibrium adsorption isotherms. The adsorption media were prepared using borate buffer

solutions of pH 10.0 containing 0.00308 M KCN. The initial concentrations of gold were varied between 5 and 50 mg of gold per litre, each point of the isotherm representing a different initial concentration. Generally, the adsorption curves were characterized by an initial rapid rise in adsorption at low equilibrium gold concentration regardless of the %CBO. This was followed by a gradual rise and then flattening of the curve at higher equilibrium concentration. The figure also shows that gold loading on the activated carbons increase with %CBO, a trend observed for all CO_2 activated carbons. However, for higher %CBO (over 75%), loading dropped drastically as exemplified by 76%CNS carbon in Figure 2. RH based carbons on the other hand, show very low adsorption capacities when compared to the other carbons. Their capacities did not differ significantly among themselves.
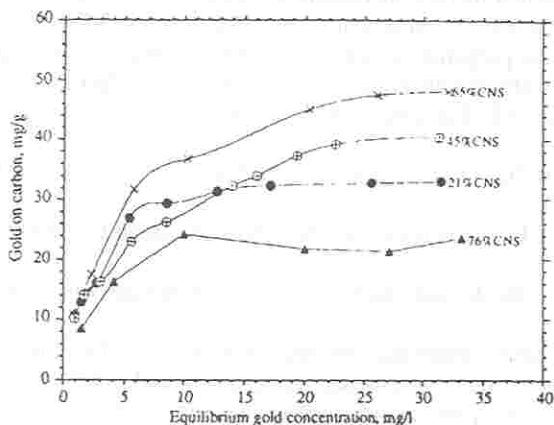
Figure 2.   Equilibrium adsorption isotherms for gold cyanide on CNS carbons (volume of solution = 100 mL, mass of carbon = 0.04 g, contact time = 24 h, temperature = 303 K).

The increase in the gold adsorption on the activated carbons with increase in %CBO may be explained to be due to the following interrelated factors:

(a) The formation of more micropores and hence an increase in surface area.
As argued earlier, increase in % CBO causes an increase in micropores. The increase may also be associated with an increase in adsorption sites. However, quantitative comparisons are difficult to arrive at since surface areas and micropore volumes include regions which are accessible to N_2 [3] but not to the large aurocyanide ions. For instance, the surface area of 65% CONS carbon is greater than that of 65% BCO by 216 m^2g^{-1}. However, their adsorption capacities differ only by 1.5 mg gold per g carbon, that of 65% BCO being higher. This may imply that there are more regions in the surface area of 65% CONS which are not accessible to the large aurocyanide ions. The drastic drop in adsorption capacity at about 75% carbon burn-off, on the other hand, may be explained by the collapse of the lattice structure of the carbon and hence loss of porosity.

(b) The maintenance of good pore structure to facilitate access of the aurocyanide ion to the adsorption sites.
It is well known that pore structure has marked influence on the accessibility of the adsorbate ions on the adsorption sites. Hence, increase in adsorption capacity with %CBO may imply that the pores created as a result of increase in %CBO do not block diffusion of the aurocyanide

ions on their way to the adsorption sites.

(c) Formation of more condensed aromatic structure.

Ibrado and Furstenau [12] found that adsorption of aurocyanide increases with aromaticity, i.e., the graphitic structure of the carbon. The adsorption is high on the edges (defects) of the graphitic planes [13]. It is an established fact that efficient activation generates a carbon with high aromaticity [3]. Adams et al. [2] have reported that the onset of aromatization occurs at 973 to 1073 K, and then increases steadily. In this study, the activation temperature was 1200 K and it was observed that %CBO increased with time of activation. Following the above argument one can conclude that the increase in %CBO at this temperature leads to increase in aromatization of the carbon thereby increasing the affinity of the carbons for aurocyanide.

The affinity of the carbons for gold is not only a function of %CBO, but also the material from which the carbon is prepared. When a comparison is made on adsorption capacities for carbons prepared from various source materials, activated to %CBO ranging from 21 to 45%, a constant trend is observed. The trend is as given below:

CNS-based carbons < BCO-based carbons < CONS-based carbons < BWC-based carbons.

However, when the %CBO is increased to about 60% the trend becomes:

CNS-based carbons < BCW-based carbons < CONS-based carbons < BCO-based carbons.

The change in the above trend may be associated with the fact that the structure of the carbon skeleton of the product, and hence the quantity and size distribution of the pores developed inside the carbon particle, are strongly dependent on the source material [5]. The variation in the trends with change in %CBO may be attributed to the fact that different source materials need different optimum activation conditions, viz., temperature and time of activation [7]. Carbons of some source materials, e.g., BWC carbons, burn off quickly hence developing the pore structure faster than others, and likewise collapse quickly. RH-based carbons, on the other hand, show the poorest gold adsorption capacity. This is probably due to the high ash content found in the carbons. Increase in impregnation ratio does not cause any appreciable change in gold adsorption.

The Langmuir and Freundlich models (equations 1 and 2, respectively) were found to correlate well the equilibrium adsorption data as exemplified in Figure 3 and 4, respectively.

$$\frac{V}{m} = kC^{\frac{1}{n}} \tag{1}$$

and

$$\frac{C}{V/m} = \frac{1}{KV_m} + \frac{C}{V_m} \tag{2}$$

where, V is the amount of adsorbate adsorbed by mass, m, of solid adsorbent, V_m is the adsorption maximum, C is the equilibrium concentration of adsorbate ions in solution, and K,

k, and n are constants.

However, the Langmuir equation is found to describe the adsorption data better than the Freundlich equation as manifested by the correlation coefficients obtained.
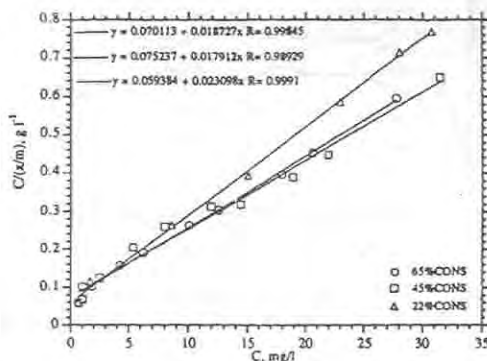

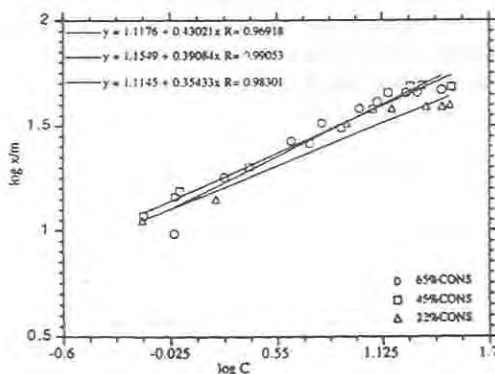Figure 3. Langmuir plots for gold adsorption on CONS carbons.

Figure 4. Freundlich plots for adsorption of gold on CONS carbons.

ii) Effect of temperature

As observed by other workers [1, 3], equilibrium gold loading on the prepared carbons decreases markedly as the temperature of the adsorption medium increases. However, Ladera et al. [3] observed that the decrease does not occur at temperatures between 298 and 308 K. The poor adsorption of gold on activated carbons at elevated temperature is associated with the increased solubility of the adsorbate in the aqueous phase [2]. It is well known that there is an increase in adsorption onto activated carbons of substances with lower aqueous solubility [4]. For instance, the solubility of $KAu(CN)_2$ in hot water is about 14 times greater than in cold water. The effect of temperature on gold adsorption is shown in Figure 5.
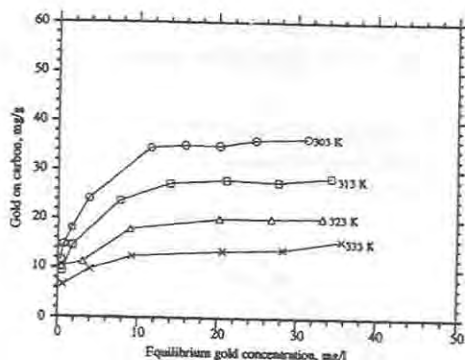
Figure 5. Equilibrium adsorption isotherms for gold cyanide on 21% BCO at different temperatures (conditions: volume of solution = 100 mL, mass of carbon = 0.04 g, contact time = 24 h).

The calculated [1] isosteric heats for the adsorption of gold on the activated carbons are shown in Table 2. It was noted that the adsorption is characterized by more exothermic reactions at low gold loadings. This result suggests that stronger adsorbent-adsorbate interactions take place at lower loadings than at higher loadings. McDougall et al. [1] reported an average value of -42 kJ mol^{-1} for the extraction of aurocyanide by activated carbons. Adams et al. [2], on the other hand, reported values of -75.0 kJ mol^{-1} and -35 kJ mol^{-1} at 20 mg gold/g carbon and 54 mg gold/g carbon, respectively.

Table 2. Isosteric heats of gold adsorption on different activated carbons.

	21% BCO				22% CONS				65% CONS			
Gold loading (mg g^{-1})	12.5	20.0	75.0	100	12.5	20.0	75.0	100	12.5	20.0	75.0	100
-q (kJ mol^{-1})	29.61	25.33	17.08	12.14	30.04	25.60	15.45	14.38	34.77	23.69	17.43	12.67

iii) *Effect of the ionic medium*
The presence of spectator electrolytes in an adsorption medium has a great effect on the adsorption process [1, 2]. In this study, the following order of enhancement in gold adsorption was observed:

no additive < borate buffer < $NaClO_4$ < KCl < NaCl < $MgCl_2$ < $CaCl_2$ < $BaCl_2$
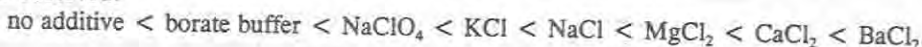
This trend is also shown in Figure 6. The above trend corresponds to increase in ionic radii [15], but only for the case of alkaline earth metals (i.e., Mg, Ca and Ba). Adams et al. [2], however, observed such correspondence for both alkali and alkaline earth metals. The increase in adsorption capacity with increase in ionic radii (for the alkaline earth metals) may be explained in terms of decrease in aqueous solubility of aurocyanide salts as the cation size increases [2]. As discussed before, adsorption increases with decrease in aqueous solubility of a substance.
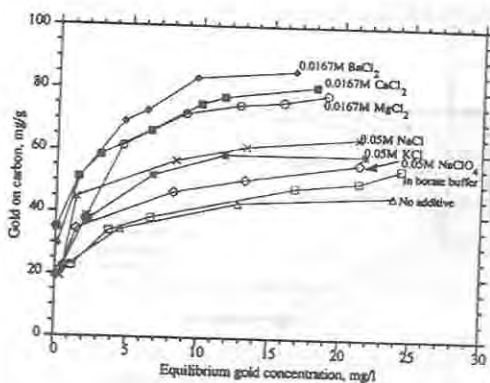
Figure 6. Equilibrium adsorption isotherms for gold cyanide on 60% CONS carbon in the presence of various additives (conditions: volume of solution = 100 mL, mass of carbon = 0.04 g, contact time = 24 h, temperature = 303 K).

The gold adsorption capacity from media containing borate buffer solution is lower than those found in the presence of other additives. Among other factors, this may be attributed to the effect of pH. The buffer solution was maintained at pH 10, while the other adsorption media were at their natural pH values which were between 6.0 and 7.5. According to McDougall et al. [1] the pH value of an adsorption medium has a great effect on gold adsorption; the process being enhanced at pH values lower than 6.

iv) *Effect of mineral impurities and treatment of the carbon with water or HCl*
Albert et al. [16] established that metal impurities found on the surface layers as well as in the bulk material of activated carbons have adverse effects on dispersion of palladium on the carbon support. The dispersion became poorer as the concentration of the surface metal impurities increased. Generally, adsorption characteristics of activated carbons from solution phases are significantly influenced by mineral impurities inherent in the carbon [17]. This suggests that the metal impurities present in the activated carbons prepared in this study also affect the gold adsorption process.

Treatment of the activated carbons with water and HCl caused a decrease of some metal impurities. The treatment also increased gold adsorption capacity as shown in Figure 7. Albert et al. [16] found that treatment of activated carbons with 1 M HCl causes a decrease in oxidic and aliphatic species on carbon surfaces and an increase in aromatic carbons. Increase in aromatic carbons causes an increase in affinity of the carbons for gold cyanide complex [13]. Figure 7 shows that the water-treated activated carbons gave a slightly higher gold adsorption capacity than the dilute HCl-treated carbons. This suggests that water treatment alone may affect the aromatic/graphitic carbons to oxygen ratio in a positive way leading to a higher gold adsorption capacity. Both water and HCl treatments remove some metal impurities and this may also lead to enhancement of gold adsorption capacity. However, the data available do not allow the establishment of a correlation between the nature of surface carbons, functional groups, metal impurities, and the adsorption of gold.
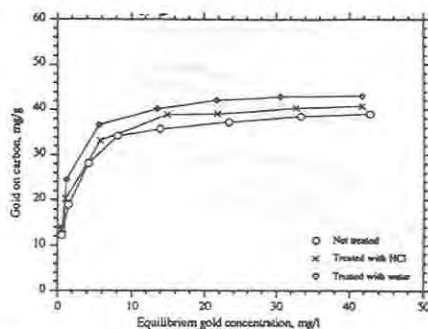
Figure 7. Effect of treating 38% BCO carbon with distilled water and HCl on adsorption of gold (conditions: volume of solution = 100 mL, mass of carbon = 0.04 g, contact time = 24 h, temperature = 303 K).
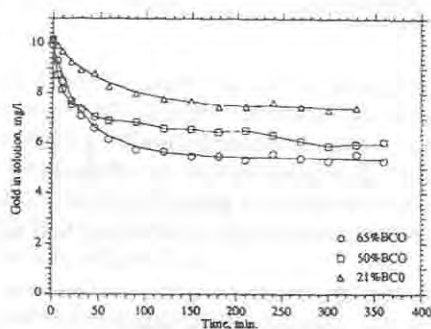

Figure 8. A curve of gold remaining in solution *versus* time for adsorption on BCO carbons (conditions: volume of solution = 800 mL, mass of carbon = 0.1 g, pH = 10.0, nitrogen atmosphere, temperature = 303 K).

Evaluation of kinetic adsorption data for gold

i) *Effect of carbon type and %CBO*. The rate of adsorption of gold on activated carbons is shown in Figure 8. Generally, the curves show a relatively rapid rise in adsorption in the first hour, followed by a decrease in rate and a very slow approach to equilibrium. The adsorption rate increases with increase in %CBO. This may be explained in terms of increase of micropores and wider pores for bituminous coal-based carbons when the level of activation is increased.

The kinetic data fit a first order kinetic equation up to about one hour. These results are in agreement with those obtained by Adams *et al.* [3]. The 65%BCO carbon shows the highest gold adsorption rate. Bituminous coal-based carbons activated to about 60% carbon burn-off posses wider pores, as explained before. Thus, possible steric hindrances of adsorbate ions are minimised, a reason as to why the bituminous coal-based carbons show high adsorption rates.

The best fit of the kinetic data was presented by the following empirical equation given by Laidera *et al.*

$$X = \frac{at}{b + t}$$ (3)

where, X is reacted fraction, t is time in minutes, and a and b are constants. The plots that are obtained based on equation 3 are shown in Figure 9.
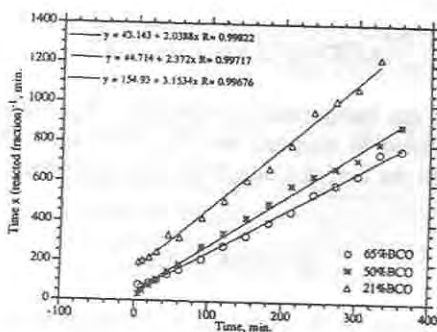

Figure 9. Plots based on a linearized form of Laidera *et al.* equation for gold adsorption on BCO carbons.

ii) *Effect of initial adsorbate concentration.* The initial metal concentration has no significant influence on the adsorption rate as well as equilibrium adsorption. This observation is exemplified in Figure 10. The results agree with those of Laidera *et al.* [3] who also found that gold adsorption is not influenced by variation of the initial concentration.
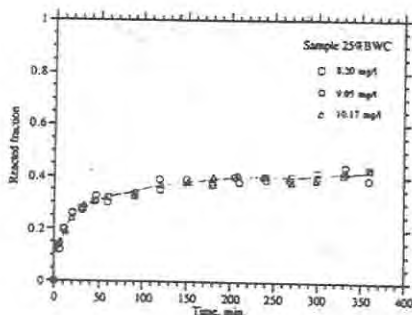

Figure 10. Effect of initial gold concentration on gold adsorption (conditions: volume of solution = 800 mL, mass of carbon = 0.1 g, pH = 4, nitrogen atmosphere, temperature = 303 K).

CONCLUSION

The activated carbons prepared from agrowastes were microporous while those prepared from a non agrowaste, bituminous coal, possessed some wider pores. However, most of the agrowaste-based carbons showed good gold adsorption capacity. Rice husk-based carbons had the poorest affinity for gold whereas the bituminous coal-based carbons had the highest adsorption capacity. The adsorption of gold was affected by the type of carbon, level of carbon burn-off, pretreatment, ionic composition and temperature. Thus, with a proper selection of

carbons and operation conditions, higher adsorption values of gold from aqueous solutions can be achieved.

ACKNOWLEDGEMENTS

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