Wastewater treatment with gold recovery through adsorption by activated carbon

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Abstract

The exploitation of gold mines of North Greece, which starts soon, and the continually increasing environmental concerns (leading to lower cyanide maximal permitted values in water), make the relative research of considerable interest. With respect to this, a refinement of the gold and silver recovery methods may contribute to cost minimisation of cyanide wastewater treatment. Several researchers have investigated the kinetics of the adsorption of gold and silver by activated carbon from cyanide, thiourea and chloride solutions. Very few works have been reported on gold adsorption by activated carbon from iodine/iodide solutions which can be obtained as a downstream leach liquor in wastewater treatment. This work investigates the kinetics of adsorption of gold from iodine solution by activated carbon. It is proved that this kind of adsorption obeys the following kinetic equation:

\[ C_b = C_0 - (C_0 - C_{\text{inf}})[1 - \exp(-kt)] \]

where \( C_b \), \( C_0 \), \( C_{\text{inf}} \) are the concentrations of gold species in the bulk solution at time \( t \), 0, \( \infty \), respectively. The values of the parameters \( C_0 \), \( C_{\text{inf}} \), \( k \) of this equation are estimated by means of non-linear least squares regression. The \( k \)-values estimated in different temperatures give (by similar non-linear regression) a region of activation energy values which indicate, at 95% confidence level, that the critical stage of the process is the diffusion of the gold species in the pores of the activated carbon.

1 Introduction

For many years, cyanide has been the main leaching medium for gold recovery either from ore or from solid waste. The mechanism of the adsorption of gold dicyanide by activated carbon has been reported by several authors [1, 2, 3].
Nevertheless, the use of cyanide has recently come under thorough re-examination because of the environmental impact of this hazardous reagent. In view of toxicity of cyanide, EU and subsequently national / regional / local authorities have been forced to impose stricter environmental regulations. Without a doubt, the best way to get rid of this environmental problem is to replace cyanide with a substitute. Such alternative lixiviants are the halogens and among them the iodine seems to be the most promising, according to several studies \[4, 5, 6, 7\], as it forms the most stable gold complex (mainly \(\text{AuI}_3\)) in aqueous solutions, even for high pH-values, according to the following network of reactions:

\[
4\text{I}_2(aq) + 4\text{I}^- \rightarrow 4\text{I}_3^- + 8\text{e}^- \\
2\text{AuI}_2 \leftarrow 2\text{Au} + \text{I}_3^- + \text{I}^- \\
\text{I}^- + 2\text{AuI}_4 \leftarrow 2\text{Au} + 3\text{I}_3^-
\]

The aim of this paper is to provide a quantitative model for the recovery of gold from iodide solutions, where there exists mainly under the form of \(\text{AuI}_3\). The adsorbing medium is activated carbon, because of its excellent adsorptive characteristics, thoroughly studied from the scientific and the technical point of view, and its relatively low price. It is worthwhile noting that the gold sorbed in the activated carbon can be recovered by many well-known methods, including desorption / leaching and ashing. The economics of these methods are not always favourable but the corresponding investment can be profitable, as the State offers a general subsidy for materials recovery which is about 40% of the initial capital. In addition, there is a specific subsidy for innovative applications of new technologies currently at a stage of R&D; gold recovery from iodide solution, instead of cyanide, can be considered as such an innovation applicable to both stages of gold life cycle, ore leaching and waste recycling. The special interest of the Greek scientific community on this matter comes from the recent governmental decision to give licence for the full exploitation of gold mines of North Greece by building a large metallurgical unit.

2 Suggested mechanism and phenomenological kinetic model

The mechanism of adsorption can be broken down into the following stages:
1. Transport of gold species (gold-iodine complex molecules) from the bulk solution towards the vicinity of a layer adjacent to the solid.
2. Diffusion of species through this layer towards the solid surface.

3. (a) Adsorption of a rather limited number of molecules on the outer surface of the solid, (b) Diffusion of the rest of the molecules into the active pores.

4. Adsorption on the inner surface of solid i.e. the bottom and the walls of micropores (of an effective radius 10-25 Å [8]).

5. Partial reduction / cementation of the adsorbed gold complex at the activated carbon surface.

Stages 3a and 3b proceed in parallel, all others in series. The time interval between adsorption and reduction is expected to be negligible. A phenomenological kinetic model can be derived as follows:

Let \( z \) be the driving force for adsorption, as a function of concentration, temperature and surface nature / topology. Under the assumption that the adsorption rate is proportional to this force, which in its turn, decreases steadily when the adsorbed amount \( L \) increases, we have the following simple relations:

\[
\frac{dL}{dt} = k_1 z \quad (1)
\]
\[
-dz = k_2 dL \quad (2)
\]

A combination of eqns (2) and (1) gives \(-dz/dt=-(dL/dt)(dz/dL)=k_1k_2z or -dz/z=k_1k_2dt\), which is easily integrated to give \(\ln(z/z_0) = -k_1k_2 t\), or \(z=z_0 \exp(-k_1k_2t)\), where \(z_0\) is the value of \(z\) at \(t=0\). By substituting the last expression for \(z\) into eqn (1), we obtain \(dL/dt=k_1z_0 \exp(-k_1k_2t)\) or \(\int_0^t dL = k_1z_0 \int_0^t \exp(-k_1k_2t)dt\) or

\[
L = (z_0/k_2)\exp(-k_1k_2t) + z_0/k_2 \text{ or }
\]

\[
\text{L} = (z_0/k_2)[1-\exp(-k_1k_2t)] \quad (3)
\]

For \(t=0, L=0\). We define \(L_{\text{inf}} = \lim L_{t \rightarrow \infty}\). Obviously, \(L_{\text{inf}} = z_0/k_2\). By introducing this asymptotic value \(L_{\text{inf}}\) into eqn (3), we obtain

\[
L = L_{\text{inf}}[1-\exp(-k_1k_2t)] \quad (4)
\]

Let \(C_b, C_{\text{inf}}, C_0\) be the concentrations of \(AuI_2^-\) in the bulk solution at time \(t, 0, \infty\), respectively. Obviously, \((C_0-C_b)V=L\) and \((C_0-C_{\text{inf}})V=L_{\text{inf}}\), where \(V\) is the volume of the solution. Therefore, eqn (4) is transformed in concentration terms as follows: \((C_0-C_b)V=(C_0-C_{\text{inf}})[1-\exp(-k_1k_2t)]\) or, for \(k=k_1k_2\),

\[
C_b = C_0 - (C_0-C_{\text{inf}})[1-\exp(-kt)] \quad (5)
\]

3 Experimental results and interpretation

The measurement of adsorption took place in an 1 L glass vessel equipped with a stirrer operating at 300 rpm to keep activated carbon in suspension. The glass
vessel, containing 0.5 L aquatic solution, was placed into a water bath to keep
temperature constant at the desired level. The granular activated carbon used was
NORIT PK 1-3 with density backwashed and drained 230 g/L, total pore volume
1.2 cm³/g, uniformity coefficient 1.9 and particle characteristic diameter (Dₚ) distribution
given by the representative values 25 % w/w for Dₚ >2.4 mm and 55%
w/w for Dₚ >1.7 mm, within the limits: max 10 % w/w for Dₚ >3.4 mm and 95%
w/w for Dₚ >0.7 mm. The concentration of gold species in the solution was
measured by means of a Perkin Elmer atomic absorption spectrophotometer.

Figure 1 depicts the recovery of gold species as a function of time of adsorption for
nine different initial concentrations of Au₁⁺, ranging from 10.2
mg/L to 92.1 mg/L. Recovery % (Rₚ) is defined as 100(C₀–Cₚ)/C₀ and the
parameter values estimation of Equation (5) was carried out by Least Squares
Non-linear Regression (LSNR). The estimates for the two extreme sets of data are
C₀=92.13 mg/L, k=0.0371 min⁻¹, Cₚ=14.56 mg/L or max recovery 84.2%
for experimental C₀=92.1 mg/L, and C₀=10.22 mg/L, k=0.0402 min⁻¹, Cₚ=0.52
mg/L or max recovery 94.9 % for experimental C₀=10.2 mg/L. The curves
Corresponding to model fitting in these two extreme sets form an envelope,
which include all experimental points of the other sets, indicating a satisfactory
resolution of results near the boundaries of the region thoroughly examined.

Figure 2 shows the dimensionless concentration ratio (Cₚ-Cₚ)/C₀, (C₀-Cₚ)
which is the complementary relative recovery (1-Rₚ), as a function of time,
where Rₚ=(C₀–Cₚ)/(C₀–Cₚ). In the same figure, the expression ln[(C₀-Cₚ)/(C₀-
Cₚ)] is also shown as the dependent variable to obtain a linearized regression
equation by transforming model (5) into ln[(C₀-Cₚ)/(C₀-Cₚ)]=−kt.

Figure 3 shows the dependence of (i) absolute initial rate |dCₚ/dt| and (ii)
kinetic constant k on initial concentration C₀ of gold species. Simple linear
models have been adopted for Least Squares Linear Regression (LSLR), as there
are not corresponding pure theoretical relations.

The above diagrams clearly show that there is a max Rₚ – value which we
must take into account for the determination of the bath depletion or recovery
rate. The influence of Cₚ on the rate becomes obvious by considering the
corresponding differential equation dCₚ/dt=−k(Cₚ-Cₚ). The fact that Cₚ
is significantly positive, although the total quantity of gold species initially existing
in the solution might be adsorbed in the pores of activated carbon to form an
incomplete mono – molecular layer (implying theoretically Cₚ=0), supports the
view that massive adsorption takes place in the pores not far from their mouth.
The building up of such an obstacle holds back the gold species, which form
adsorbed multilayers on the outer surface and the low depth inner surface,
implying decrease of the driving force z which asymptotically approaches zero.

Figure 4 gives the results obtained by measuring adsorption on different
quantities C of activated carbon. The first of them shows that there is a very
good fitting of model (5) to experimental results. All three – parameter values
have been estimated by means of LSNR, i.e. no one of them has been set
exogenously in the regression equation. In all cases, the endogenous estimate of
C₀, i.e. Cₚ at t=0, coincides with the value set a priori and measured by the same
technique which was used for measuring Cₚ at any time t. The rate constant k is
Figure 1: Dependence of recovery (%) on time of adsorption for nine different initial concentrations of gold iodide (25°C, 1g activated carbon). The solid lines have been drawn through LSNR of the original kinetic model by fitting to the data representing the two extreme experimental cases.

Figure 2: Dependence of dimensionless concentration ratios on time of adsorption, for initial concentration 50.1 mg/L (25°C, 1g activated carbon). The parameter – values of the solid curve have been estimated through LSNR. The straight line has been derived as a result of LSLR of the linearized model.
Figure 3: Dependence of (i) absolute initial rate $\left| \frac{dC_0}{dt} \right|$ and (ii) kinetic constant $k$ on initial concentration $C_0$ of gold iodide ($25^{\circ}C$, 1g activated carbon). The straight lines have been derived as a result of LSLR.

![Graph showing the dependence of absolute initial rate and kinetic constant on initial concentration.]

Figure 4: Change of gold iodide concentration as a function of time of adsorption, for different activated carbon quantities added ($C_0=50\pm0.1$ mg/L, $25^{\circ}C$). The parameter – values of the solid curves have been estimated through LSNR.

![Graph showing the change of gold iodide concentration over time for different activated carbon quantities.]

Proportional to the amount $C$ of activated carbon used, as we obtained by LSLR the relation $k=0.0026+0.0403C$ with $R^2=0.9926$ and 95% confidence region (i) for slope $(0.0355) - (0.0451)$ and (ii) for intercept $(-0.0068) - (0.0120)$. The
inclusion of zero within the 95% confidence interval of the intercept supports the view that there exists simple proportionality.

Figure 5 shows a representative case of \( k \) vs. \( C_{inf} \) contours for three joint confidence intervals of the model (5), with parameter – values estimated through LSNR, corresponding to the equation \( C_b=50.12-(50.12-4.4665)[1-\exp(-0.03839t)] \). The oblique orientation of the ellipses implies that the parameter – estimates are positively correlated.

The activation energy \( E_a \) of adsorption is determined by applying the Arrhenius equation to a set of five rate constants \( k_j \), estimated for five different temperatures \( T_j=288, 298, 308, 318, 328 \) K \( (j=1, ..., 5) \). To obtain results comparable to categorized data cited in literature, we set \( C_{inf}=0 \), so that \( k \) is the unique rate controlling parameter. The parameter – values, estimated through LSNR are \( E_a=4.025 \) kJ/mol=0.966 kcal/mol and \( A=0.1173 \) min\(^{-1}\), where \( A \) is the pre-exponential factor of the Arrhenius equation. The order of magnitude of \( E_a<4 \) kcal/mol suggests diffusion of gold species in the pores as the rate controlling stage. The \( E_a \) vs. \( A \) contours for three joint confidence intervals (see Figure 6) show that (i) even for the 90% ellipse the relative deviation as regards \( E_a \) is adequately small (±11.7%) and (ii) the parameter – estimates are positively correlated.

Figure 5: Presentation of \( k \) vs \( C_{inf} \) contours for three joint confidence intervals. The point \( (0.0384, 4.4665) \) has been estimated through LSNR \( (C_0=50.1 \) mg/L, 25\(^o\)C, 1g activated carbon).
4 Derivation of an explanatory model

Instead of using the phenomenological model (5), we can derive an explanatory one in order to (i) connect mass balances with kinetic expressions and (ii) incorporate the experimental results obtained into the corresponding theoretical framework. The mass balances of the gold species at the liquid – solid interface and in the bulk solution yield the following relations:

\[
\frac{dC_b}{dt} = -\frac{S k_{mA}}{V} [(C_b - C_1) - (C_s - C_2)]
\]

(6)

\[
\frac{dC_s}{dt} = n \frac{S k_{mA}}{V} [(C_b - C_1) - (C_s - C_2)] - n \frac{S D_e k_s}{V} (C_s - C_2)
\]

(7)

where:

- \( V \) is the volume of the bulk solution, \( V = n v, n \in \mathbb{R}^+ \)
- \( v \) is the volume of the layer adjacent to the solid
- \( S \) is the total outside surface area of the solid
- \( C_b \) is the concentration of the gold species in the bulk solution at time \( t \)
- \( C_s \) is the concentration of the gold species at the liquid solid interface
- \( k_{mA} \) is the mass transfer coefficient
- \( D_e \) is the effective diffusivity of gold species in the micropores
- \( k_s \) is a kinetic constant
- \( C_1, C_2 \) are asymptotic values of \( C_b, C_s \) for \( t \to \infty \)

Figure 6: Presentation of Arrhenius \( E_a \) vs \( A \) contours for three joint confidence intervals. The point \((4.025, 0.1173)\) has been estimated through LSNR \((C_{01}=0, C_0=50\pm0.1 \text{ mg/L, 1g activated carbon})\).
This system of differential equations can be easily solved to give

\[
C_b = C_1 + \left( \frac{(C_{b0} - C_1) + 2(C_2 - C_{s0})k_{mA} + n(C_1 - C_{b0})(k_{mA} + D_e k)}{2\sqrt{D}} \right) \{ \exp\left[-\frac{E - \sqrt{D}}{V} St\right] - \exp\left[-\frac{E + \sqrt{D}}{V} St\right] \} + \\
\frac{(C_{b0} - C_1)}{2} \{ \exp\left[-\frac{E + \sqrt{D}}{V} St\right] + \exp\left[-\frac{E - \sqrt{D}}{V} St\right] \}
\]

(8)

where \( E = k_{mA} + nk_{mA} + nD_e k_s \) and \( D = 4nD_e k_s k_{mA} + E^2 \)

\( C_{b0}, C_{s0} \) are the initial values of \( C_b, C_s \) at \( t=0 \).

As common values of \( n \) are expected to be very high [9] and \( D_e, k_s \gg k_{mA} \) [10], the expression above is simplified to the following relation, which is the explanatory form of model (5).

\[
C_b = C_1 - \frac{1}{2}(C_{b0} - C_1)k_{mA} + (C_2 - C_{s0})k_{mA} + (C_1 - C_{b0}) \} \exp\left[-\frac{D_e k_s k_s}{V} St\right]
\]

(9)

This kinetic model is quite general and the values of any three parameters can be estimated through LSNR, provided that the values of the rest of them are determined exogenously either by measuring the corresponding magnitudes experimentally or by calculating them independently. On the other hand, some kinetic models cited in literature can be deduced as special cases of our model. E.g., for \( C_1 = C_2 = 0 \), eqn (9) is reduced to a form similar to the kinetic model derived by Meng and Han [10].

5 Conclusions

The replacement of cyanide by iodide ion as gold complexing agent in both stages of gold life cycle, ore leaching and waste recycling, is further supported in this study. By this replacement, two targets are achieved: gold recovery from waste and substitution of the environmentally hazardous cyanide compound.

The recovery of gold from its iodide aquatic solution by means of adsorption on activated carbon follows a first order kinetic model with a positive asymptote \( L_{inf} \), implying that the rate of recovery \( dL/dt \) does not depend only on the rate constant \( k \). The validity of such a two - parameter differential equation as kinetic model, resulting in a three - parameter integrated function, can be attributed to partial blockage of active micropores due to massive adsorption of gold species on the inner surface relatively near the mouth of these pores. This blockage inhibits the diffusion into the deeper section (i.e. near the bottom of the pores), thus decreasing the surface available for adsorption / recovery. This is a critical issue influencing both, the maximum recovery of gold and the rate of process, as the diffusion in the pores is most likely the controlling stage; this claim is further supported by the very low activation energy (approx. 1 kcal/mol)
we found by applying the Arrhenius equation on $k$ – values estimated within the temperature region $15$ – $55$ °C.

Last but not least, we derived a phenomenological and an explanatory model for this kind of recovery by adsorption. The former is based on the concept of adsorption as a potential function of concentration, temperature and surface nature / topology. The second model relates mass balances (i) of the gold species at the liquid – solid interface and (ii) in the bulk solution with kinetic expressions while incorporating the experimental results into the corresponding theoretical framework.

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References


