

Gold Adsorption In Thiosulfate Solution Using Anionic Exchange Resin

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Abstract— Gold adsorption was studied with $(\text{NH}_4)_2\text{S}_2\text{O}_3$, using NH_4OH as pH regulator, in an ion exchange resin AuRIX[®]100, evaluating the adsorption stage, the experiments were carried out in a batch tests and ion exchange column. It was found NH_4OH , maximizes the adsorption of gold at pH 10.5 and the presence of thiosulfate, it is favorable for the adsorption of the gold to 99%. In column tests the adsorption is achieved to a 75% of gold. In the model of adsorption the experimental data were adjusted to the Freundlich isotherm. The AuRIX[®]100 resin is efficient; it has a higher capacity and fast kinetic and the results of experiments at room temperature favor the kinetic adsorption process.

Keywords— Adsorption, Anion Exchange Resin, Gold, Thiosulfate

I. INTRODUCTION

Studies in literature about the use of resins for the recovery of gold from aqueous solutions with thiosulfate and ammonia [1], where using resins of weaker base and stable species extracted is the complex gold-thiosulfate, anions existing in aqueous solution, such as sulfite, trithionate and tetrathionate which are adsorbed by the resin, causing a decrease in the complex $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$.

In investigations of gold adsorption using Amberlite resin IRA-410 in medium thiosulfate-ammonia, it was shown that the adsorption of gold was rapid, the presence of thiosulfate strongly disfavored the adsorption and the presence of ammonia, however it did not affect mostly; therefore, this aspect is not very clear [2].

So that studies realized to evaluate the efficiency of the resin AuRIX[®]100, for the recovery of complex gold-cyanide at (pH=10.7), it was determined that increasing the solid-liquid ratio the amount of gold per unit mass of resin increases proportionally as was shown by Valenzuela et al. [3]. During the adsorption of gold have evaluated various materials obtained 428 mg g^{-1} resin Amberjet[™]4400, 170 mg g^{-1} in activated carbon and 362 mg g^{-1} between biosorbent as was investigated by Seob et al. [4]. There is great interest

in proposing alternative to cyanide leaching for gold extraction, less toxic compounds and seeking viable techniques for maximum extraction of precious metals [5].

The recovery of silver from thiosulfate and thiocyanate leach solutions on the sorbents investigated in anion exchangers in thiosulfate solutions (pH=10.6) recovery with AV-17-10P (93%), AN-85-10P (68%) and AN-25 (69%), in thiocyanate solution (pH=2.2) AV-17-10P (88%), AN-85-10P (73%) and AN-25 (78%). It can be seen that LK-4 and AV-17-10P have the best adsorption characteristics and hence were selected for further investigations, [6]. Although cyanide is an effective leaching agent for gold extraction, high cyanide consumption makes the cyanidation unfavorable for copper rich gold ores, [7]. In this regard, thiosulfate is often promoted for the treatment of copper rich gold ores, [8].

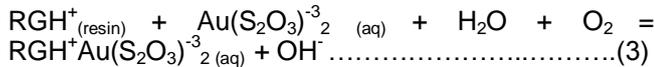
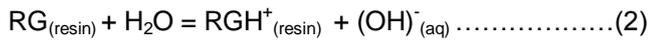
In the presence of ammonia there was a concentration which maximized the adsorption of gold, while thiosulfate and impurities presence was harmful for the adsorption of gold. During elution, ammonia favored the process as long as thiosulfate showed a maximum starting from which the elution diminishes.

The effect of the pH regulator was very important; it was revealed that when the pH was regulated with caustic ammonia, a synergic effect appeared which favored the elution. Temperature favored the elution process, the presence of ammonia favors the adsorption of gold at 0.6 M of NH_3 as was specified by Vargas et al. [9]. That gold adsorption was very fast, the copper was in a certain measure a competitor of the gold, but its biggest negative effect was that acted as catalyst of the oxidizing reaction of thiosulfate to tetrathionate and trithionate, this effect was shown by Bas et al. [10].

The ion-exchange process can also be used to increase the concentration of metal ions in a solution. The metals are extracted from solution onto an appropriate ion-exchange resin. Elution of the loaded resin bed under pre-determined conditions can the yield an eluant that has a metal concentration higher than that of the solution from which the resin was loaded. The reactions performed with gold-thiosulfate and anion resins, are represented as follows:



Adsorption:



Where: $H_{(aq)}$: aqueous solution, G: guanidine. R^+C^- : functional group into an anionic exchanger, R^+ : fixed ion in the functional group C^- : exchangeable anion in the resin and D^- : exchangeable anion in the solution and the indexes (resin) and (aq) denote that the ion exchanger is in (or resin) or in the solution respectively.

II. EXPERIMENTAL PROCEDURES

A. EXCHANGE RESIN AURIX®100

The resin AuRiX®100 ion exchange resin is based on a styrene di-vinylbenzene based macroporous resin bead functionalized with guanidine groups, it extracts the gold-thiosulfate complex, it is of a strongly alkaline nature, with particle size (% < 0.60 mm) 0.01, of appearance tan spherical beads and of a yellow color, recommended gold loading in adsorption (2000-10000 g ton⁻¹), volume capacity (0.25-0.35 eq-L⁻¹), the selectivity while quite selective for gold AuRiX®100 will extract other anionic metal gold-thiosulfate complexes. The order of extraction is as follows: Au > Ag > Zn ~ Ni > Cu > Co > Fe. The observed selectivity is to some extent dependent upon pH of the incoming aqueous feed solution as might be expected for an ion pair extraction type mechanism.

B. Adsorption Stage

1) Gold Adsorption Stage in Batch System

The tests were performed in batch system in a stirred reactor, variable rate up to 800 min⁻¹, at room temperature, using an AuRiX®100 resin. The equipment used was a glass reactor Pyrex brand, capacity 2 L, adding to the reactor aqueous solution (500 mL) with different initial concentrations of gold and (NH₄)₂S₂O₃ at room temperature by adjusting pH with NH₄OH, ratio resin/dissolution of 10 mg L⁻¹, at different rates, taking 10 mL samples for analysis every 0.5 h, pH was measured, in 3 h the stirring was stopped, gold in aqueous solution was analyzed by atomic absorption technique in Perkin Elmer Analyst 400 atomic absorption spectrometer, experimental parameters are shown in Tab. 1, in order to evaluate the gold adsorbed versus time, and the gold loading on the resin was determined by mass balance [11].

TABLE 1. Variables and ranges of experimentation in the stage for batch adsorption tests [12]

Variables	Ranges of Experimentation
Stirring speed (min ⁻¹)	200-800
Contact time (h)	0-3
Temperature (°C)	25-45
[(NH ₄) ₂ S ₂ O ₃] (M)	0.00674-0.04
[Au] _i (mg L ⁻¹)	1-8
[NH ₄ OH] (M)	0.30-0.81
pH	9-10.50

2) Gold Stage Adsorption Column System

Column tests of ionic exchange divided into 4 sections serially connected, solid-liquid separation with an aqueous suspension and resin at each stage, each section has a wire mesh at the lower and upper parts to retain the resin placed in each one of the cells, to pass the gold-containing solution through the column a peristaltic pump was used in three experimental runs, with 5 g of resin as stationary phase at 25°C, at rates of 0.50, 0.60, 0.70 min⁻¹, with 7.43, 15, 23 mL min⁻¹, equivalent to 89-276 BV/h, it was necessary to know the flow of solution/volume resin ratio and the adsorption isotherms were also analyzed. In figure 1, the experimental scheme of the stage of adsorption in a batch system and the ion exchange column are shown.

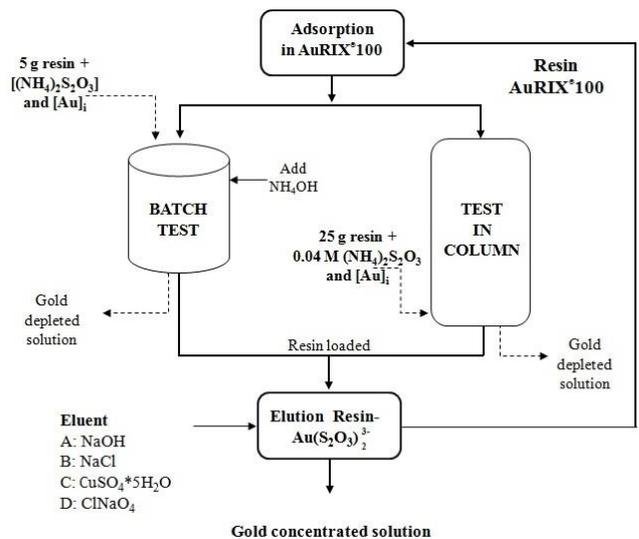


Fig 1: Experimental diagram for gold adsorption.

C. Calculation of Resin Loading Capacity (Equilibrium Isotherm)

The rates and equilibrium of gold thiosulfate adsorption depends upon the loading of gold already on resin, depends on the number of sites available. As the resin becomes loaded it is slower to take up gold and concentration of gold in equilibrium increases. The activity of resin falls off exponentially as gold is adsorbed and thus resembles the behavior of catalysts or solids which adsorb gasses or organic molecules. These materials follow Freundlich isotherms and give a straight line plot of log ([Au]_i) versus log ([Au]_s).

D. Adsorption Model

1) Freundlich Adsorption Model

The isotherm Freundlich was one of the first equations proposed to relate the amount adsorbed with the concentration of material in the solution. The surface of the solids in their structure in many cases is heterogeneous. For this reason the heat of adsorption is not uniform on the surface, Freundlich proposed an empirical relationship for the isotherm of the form:

$$q_e = KC_e^{1/n} \dots\dots\dots(4)$$

Where q_e and C_e are the amount of adsorbate adsorbed per unit of weight of the adsorbent, is the concentration adsorbate's balance in the solution after adsorption, K charge capacity of the resin and $1.n^{-1}$ is the intensity of adsorption [13] [14].

E. Effect of the Initial Gold Concentration

If the adsorption rate is not influenced by the equilibrium loading capacity then the rate of gold depletion from solution and therefore the rate of gold adsorption onto resin can be modeled with a first order rate equation as follow:

$$\frac{d[Au]_s}{dt} = K[Au]_s = \frac{V_r d[Au]_r}{V_s dt} \dots\dots\dots(5)$$

Where $[Au]_r$: concentration of gold on resin ($mg\ g^{-1}$), $[Au]_s$: concentration of gold in solution ($mg\ L^{-1}$), K : rate constant ($1.t^{-1}$), V_s = volume of solution and V_r : volume of resin. A first order rate equation can be integrated with respect to time and the rate constant determined graphically from a plot of $-\ln ([Au]_s/[Au]_{s0})$ versus time. This plot should give a straight line with K equal to the slope.

$$-\ln \frac{[Au]_s}{[Au]_{s0}} = kt \dots\dots\dots(6)$$

An method for determining the extraction kinetics of the resin is the Model of Fleming, by Nicol et al. [15], to calculate the kinetic constant, the adsorption of gold from solution onto resin.

$$[Au]_r = K[Au]_s t^n \dots\dots\dots(7)$$

Where $[Au]_r$: concentration of gold on resin ($mg\ g^{-1}$), $[Au]_s$: time weighted average concentration of gold in solution ($mg\ L^{-1}$), K : Fleming rate constant ($1.t^{-1}$), t : elapsed time (h) and n : equilibrium loading factor.

III. RESULTS AND DISCUSSION

A. ADSORPTION ION EXCHANGE RESIN

In the stage of adsorption behavior of the parameters of adsorption, the adsorption tests were made of gold on the ion exchange resin of the anionic type is of strong base AuRiX[®]100 laboratory scale batch and column level. The variables studied were pH (NH_4OH), temperature, concentration of gold, ammonium thiosulfate and stirring rate (min^{-1}).

1) Reaction time

An increase in the gold extraction was achieved in 3 h, using concentrations of $1\ mg\ L^{-1}$ of gold recovery of 99%, $2\ mg\ L^{-1}$ with a recovery of 93% of gold and $8\ mg\ L^{-1}$ with a recovery of 95.75% gold [11].

2) Initial gold concentration

In the pH studies it was found that gold adsorption during the first hour is fast, reaching approximately a 99% recovery of gold and the balance in 3 h. In terms of the final adsorption obtained, the gold adsorption is dependent on pH in the range of 9.5-11.5 when gold solutions do not contain dissolved copper, but within the first 0.5 h there is a greater velocity of adsorption to pH higher to 10.5. Once reached the amount of

gold adsorbed was practically the same in all cases for the resin.

3) Agitation speed

In order to establish the appropriate stirring speed for a period of 3 h, the following gold recoveries were obtained at $200\ min^{-1}$ (98%), $500\ min^{-1}$ (99%) and $800\ min^{-1}$ (95%), [12].

4) Thiosulfate concentration in gold adsorption

At lower concentrations of thiosulfate in the solution the lower is the gold adsorption of this element in the resin. In working conditions may be occurring oxidation of thiosulfate to tetrathionate and trithionate, being this last component a strong competitor of gold, for instance, coadsorption is produced, resulting in the reduction of the load of gold in a time of 3 h gold recovery was obtained at different concentrations of thiosulfate to 0.0064 M (98%), 0.03 M (98%) and 0.04 M (99%).

5) Ammonium hydroxide concentration

To resin, the gold adsorption is highly affected by the presence of ammonium hydroxide, as shown in Table 2. gold-thiosulfate complex is stable in the studied experimental conditions, which was determined by speciation analysis performed to the system, in a time of 3 h was obtained with a recovery of 0.292 M NH_4OH (99%), [11].

TABLE 2. Influence of NH_4OH on gold adsorption

[Au] _i (mg L ⁻¹)	Gold adsorption, (%)			
	pH=9	pH=9.5	pH=10	pH=10.5
1	80	90	95	99
2	91.5	89.5	89	93
8	92.2	93.6	94.6	95.7

6) Effect of pH

The effect of pH was studied at various concentration levels of gold in the range pH 9-11, as shown in Table. 3. By increasing the concentration of copper, gold complex adsorption decreases, since copper is coadsorbed along with gold by the resin. On the other hand in pH 9 the oxidation of thiosulfate to tetrathionate and trithionate with the aid of copper that acts as a catalyst occurs because the tetrathionate, is a strong competitor of gold and occupies active sites of the resin. This effect is minimized by operating at pH 10.5, because the stability of thiosulfate in the aqueous solution increases, whereby the adsorption of gold alone is affected by the competition of copper, the results at 3 h show that at different pH, gold recovery was achieved, and at pH 10.5 (99%), [11].

TABLE 3. Influence of pH on gold adsorption in 3 h.

[Au] _i (mg L ⁻¹)	Gold adsorption, (%)			
	pH=9	pH=9.5	pH=10	pH=10.5
1	80	90	95	99
2	91.5	89.5	89	93
8	92.2	93.6	94.6	95.7

B. Gold Adsorption in Ionic Exchange Column

The ion exchange operation is habitually performed semi continuously in a fixed bed of resin, through which a dissolution flows, the results are shown in Tab. 4. Concentration of gold in the resin as a function

of contact time at 25°C and initial concentration of gold of 1 mg L⁻¹.

TABLE 4. Analysis of the column in each range of time ([Au]_r=mg L⁻¹)

Time (h)	Au (in)	Au (out)	Au (adsorbed)
0	0	0	0
1	0.4458	0.0757	0.3700
3	0.8916	0.2942	0.5973
6	1.3374	0.5483	0.7890
9	1.3374	0.4814	0.8559
12	1.3374	0.4279	0.9094
25	5.7954	0.869	4.9260
Total	11.145	2.697	8.447

Using the AuRiX[®]100 resin in the continuous system a 75.8% of gold is recovered.

C) Analysis of Adsorption Isotherms

Kinetic modeling of the adsorption isotherms of the Freundlich model parameters $K = 0.33 \text{ mg g}^{-1}$, $1/n = 0.43$ and $R^2 = 0.82$, in 3 h, the experimental data were fitted to the isotherm of Freundlich (Fig. 2). Usually adsorption data are discussed and explained with adsorption isotherms [14].

1) Freundlich Adsorption Model

The Freundlich model can be expressed as eq. (4), the linear model expressed in logarithmic form, plotting $\log q_e$ versus $\log C_e$ a straight line is obtained when this is set to a Freundlich isotherm. It has been found that this equation is the best correlating experimental data in the regions where multiple layers of adsorbed molecules; this type of adsorption systems is presented by ion exchange adsorption.

2) Effect of Initial Gold Concentration

If the adsorption rate is not influenced by the equilibrium loading capacity then the rate of gold depletion from solution and therefore the rate of gold adsorption onto resin can be modeled with a first order rate in eq. (5), a first order rate equation can be integrated with respect to time and the rate constant determined graphically from a plot of $-\ln ([Au]_s/[Au]_{s0})$ versus time. This plot should give a straight line with K equal to the slope the eq. (6). En la Fig. 3 show the depletion of gold in solution with time, the value of $K=1.5$, if $K>1$ the equilibrium is displaced towards the formation of the gold-thiosulfate complex (products), the values of K change with temperature and it does not depend on initial gold concentration.

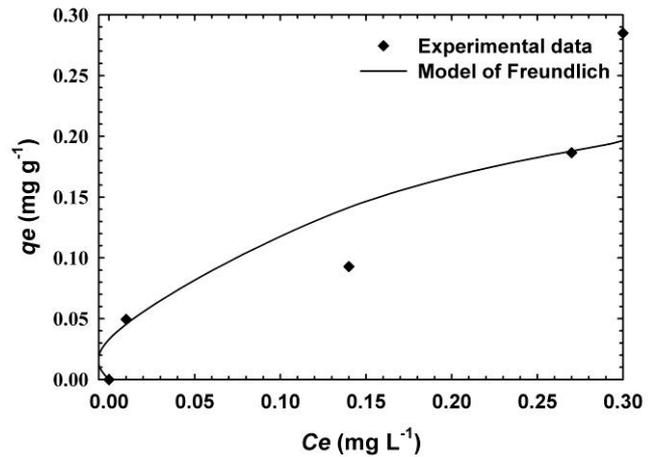


Fig. 2: Adsorption isotherm for gold in t=3 h, pH= 10.5 and T= 25°C.

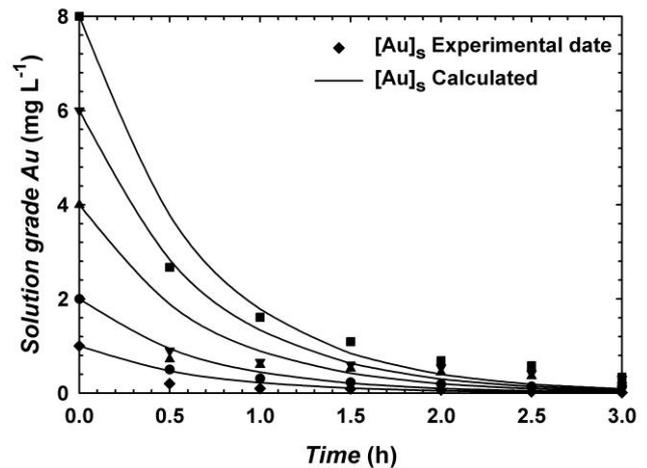


Fig. 3: Rate of disappearance of gold solution [Au]_s=1, 2, 4, 6, 8 (mg L⁻¹), experimental data (points) and Model [Au]_s= calculated (line).

An extraction method for determining the kinetics of the resin is Model of Fleming as specified by Nicol et al. [15] and Saad et al. [16]. In the kinetic the condition is the loading factor of equilibrium n , will approach to 1.0, allowing the Fleming equation to be simplified to equation of first order. The \ln becomes equation $[Au]_r = \ln k + \ln [Au]_s$, where $k = 1.542$ and $n = 0.352$, as shown in Fig. 4. The eq. (7) describing the kinetic of the extraction of the resin in the given conditions and parameters for the model are the following:

$$[Au]_r = 1.542 Au_s t^{0.352} \dots\dots\dots(8)$$

The Equation proposed by Nicol, Fleming and Cromberge is more complete and reliable for predicting gold extraction.

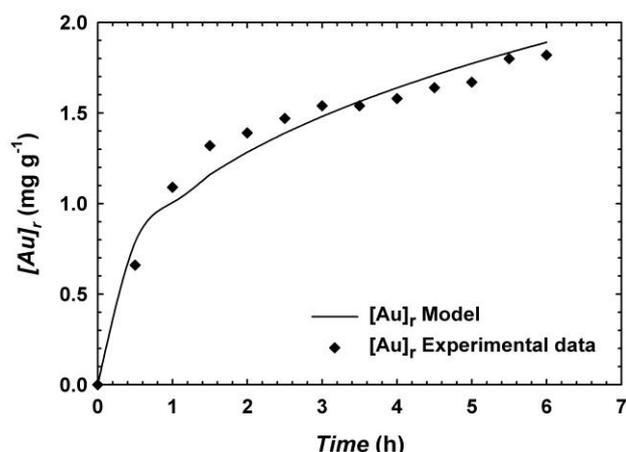


Fig. 4: Loading kinetics of resin AuRIX[®]100, in 2 mg L⁻¹ of gold.

IV. CONCLUSIONS

The dissolution of gold in the system is favorable, at the stage of adsorption pH conditions of 10.5, concentration of (NH₄)₂S₂O₃ 0.04 M, time 3 h, stirring rate 500 min⁻¹, the concentration of NH₄OH 0.292 M and 25°C.

The presence of ammonium hydroxide improves adsorption of gold, finding the best performance at a concentration of 0.292 M of NH₄OH. At lower values of gold adsorption process is damaged, there is a great dependence on pH and the adsorption of gold complex in thiosulfate resin.

It was found that the presence of thiosulfate favors the adsorption of gold. With 0.04 M ammonium thiosulfate, a 99% was obtained while adsorption with 0.0064 M of thiosulfate adsorption decreased to 98% in 3 h.

The AuRIX[®]100 resin suffers a minimal osmotic shock, always in an alkaline medium in the adsorption (pH=10.5). The AuRIX[®]100 resin experiences thermal shock at a temperature higher than 60°C in desorption.

The kinetic is favored at room temperature and increases the concentrations of (NH₄)₂S₂O₃, which are represented in the mathematical model. Model validation shows a good approximation to the experimental data, with a correlation around 0.97 and allows us to simulate the adsorption of gold. The Freundlich model fits the experimental data typically it represents in adsorption systems by ion exchange.

The gold concentration does not affect the value of K, and is not dependent on the initial concentration, its value changes with temperature, the value was K= 1.5 if K> 1, the balance is shifting towards gold-thiosulfate complex formation (product).

The equation Nicol, Fleming and Cromberge is more complete and reliable for predicting the extraction of gold, giving values of k= 1.542 and n= 0.352.

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References

- [1] E. Molleman and D. Dreisinger, *Hydrometallurgy*. **2002**, 66, 1–21. DOI.org/10.1016/S0304-386X(02)00080-4
- [2] P. Navarro, C. Vargas, V. Revenco y J. Orellana, *Rev. de Metal.* **2006**, 42 (5), 354-366. DOI:10.3989/revmetalm.2006.v42.i5.33
- [3] A. Valenzuela, J. L. Valenzuela, S. Aguayo y J. R. Parga, *GEOMIMET*. **2006**, 268, 26-38.
- [4] I. Seob, M. A. Bae, S. Wook, J. Mao, K. Sneha, J. Park, M. Sathishkumar, and Yeoung-Sang Yun, *Chem. Eng. J.* **2010**, 165, 440-446. DOI.org/10.1016/j.cej.2010.09.027
- [5] S. Syed, *Hydrometallurgy*. **2012**, 115-116, 30-51. DOI.org/10.1016/j.hydromet.2011.12.012
- [6] O. N. Kononova, A.G. Kholmogorov, N.V. Danilenko, N.G. Goryaeva, K.A. Shatnykh and S.V. Kachin, *Hydrometallurgy*. **2007**, 88, 189–195. DOI.org/10.1016/j.hydromet.2007.03.012
- [7] D. Muir, *Miner. Eng.* **2010**, 24, 576-572. DOI.org/10.1016/j.mineng.2010.08.022
- [8] D. Feng and V. Deventer, *Hydrometallurgy*. **2011**, 106, 38-45. DOI.org/10.1016/j.hydromet.2010.11.016
- [9] C. Vargas, P. Navarro, E. Araya, F. Pavez and F. J. Alguacil, *Rev. de Metal.* **2006** 42 (3), 222-233. http://hdl.handle.net/10261/2125
- [10] A. D. Bas, E. Ozdemir, E. Y. Yazici, O. Celep and H. Deveci, *15th Conf. on Environ. and Miner. Proc*, May **2011**.
- [11] M. E. Chaparro, J. L. Valenzuela, G. Tiburcio y J. R. Parga, *Inf. Technol.* **2012**, 23 (2), 53-60. DOI: 10.4067/S0718-07642012000200007
- [12] M. E. Chaparro, *M.Sc.Thesis*, Universidad de Sonora, Hermosillo, México **2008**.
- [13] I. Langmuir, *J. Am. Chem. Soc.* **1999**, 40, 1361-1403. DOI:10.1021/ja02242a004
- [14] G. Tchobanoglous and F. L. Burton, *Wastewater Engineering: Treatment, Disposal and Reuse*, 3rd ed., McGraw-Hill, New York **2006**.
- [15] M. J. Nicol, C.A. Fleming and G. Cromberge, *J. S. Afr. Inst. Min Metall.* **1984**, 84 (2), 50-54.
- [16] S. M. Saad, S. Nasser and H. A. Awaad, *J. Rad. Nuv. Chem.* **2006**, 269, 135-140. DOI:10.1007/s10967-006-0242-2