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Gold recovery in aqueous medium by cassava peels *(Manihot esculenta)* modified with citric acid

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Abstract

Cassava peels were modified with citric acid by reacting the dried and milled peels with an aqueous solution of citric acid at 60 °C and sulfuric acid as catalysts, and subsequent heating at 150 °C for completion of the reaction. The synthetic solutions were preparing taking 0,5 g of metallic gold and dissolving it in a solution of 8 ml of HNO_3 0,1 M; volume was completed until a solution of concentration in gold of 500 mg/L was reached. The influence of variables such as the initial gold concentration, temperature, and pH of the samples were analyzed in order to determine the optimum conditions in the recovery process. Experiments were carried out in Erlenmeyers in batch mode using an orbital shaker. The activation energy of the adsorption process was calculated as 157 ± 14 kJ/mol. Gold removal values were found up to 99,58%, at a temperature of 45 ° C and pH of 10, these being optimal conditions.

Keywords: Metal removal, Adsorption capacity, Gold mining, Adsorbent, Chemical modification, Cassava peel, Biomass, Citric acid, Kinetic study, Thermodynamic study.

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Recuperación de oro de soluciones acuosas por medio de cáscara de yuca *(Manihot esculenta)* modificada con ácido cítrico

Resumen

La cáscara de yuca se modificó con ácido cítrico haciendo reaccionar la cáscara seca y molida con una solución acuosa de ácido cítrico a 60°C y ácido sulfúrico como catalizador, y posterior finalización de la reacción a 150 °C. Se prepararon soluciones sintéticas disolviendo 0,5 g de oro en una solución de 8 ml de HNO_3 0,1 M y, posteriormente, se completó el volumen para obtener una concentración de oro de 500 mg/l. Se analizó la influencia de variables tales como la concentración inicial de oro, temperatura y pH durante el proceso de remoción para determinar las condiciones óptimas del proceso de recuperación. Los ensayos se realizaron en erlenmeyers con un agitador orbital discontinuo. Los datos de equilibrio y cinético se ajustaron a varios modelos comúnmente usados en la literatura.

Palabras claves: Remoción de metales, Capacidad de adsorción, Minería del oro, Adsorbente, Modificación química, Cáscara de yuca, Biomasa, Ácido cítrico, Estudio cinético, Estudio termodinámico.

1. Introduction

Gold mining is a very important worldwide industry. Global sales from gold amounted to 395 billion U.S. dollars in 2020 (Garside, 2021). This industry has a profound influence on environmental, social, political, security, and economic aspects of the society. The gold mining sector has brought economic benefits to Colombia, but also it has led to the proliferation of illegal gold mining and the emergence in the southeast of Colombia of other mineral exploitations, giving rise to irreversible damage to the environment, affection to the health of the population in places where this type of process is carried out, it has disturbed the social equilibrium, and even the national security (Ortiz-Riomalo & Rettberg, 2018). The exploitation of these deposits is destroying fertile lands, natural and forest reserves and contaminating water sources because, in most cases, they are carried out in an anti-technical way (Leal Esper, 2019).

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Gold mining is facing several challenges associated with environmental, social, economic, and technical issues. There is a need for the development of new techniques and tools that allow a greener exploitation of the mineral and that can cope with lower concentrations of gold and the increasing complexity of the deposits (Salminen et al., 2015). Current extraction technology of gold includes the use of concerning materials, such as mercury and cyanides, and involve extreme acid streams (Syed, 2012). Some studies have shown that the recovery of precious metals using biomass are more efficient than other processes, not only for tailoring streams in mining, but also for the recovery of metals from wastes (Das, 2010).

Several biomasses have been evaluated as potential adsorbents of gold and other minerals, such as seaweed (Lodeiro & Sillanpää, 2013), bacteria (Bustos et al., 2018), and fungi (do Nascimento et al., 2021). Usually, biomasses are chemically modified using several strategies, i.e., (Choudhary et al., 2018) y (Zhou et al., 2017) modified lignocellulosic and bacterial biomass with polyethylenimine, respectively. In our lab, cassava peel (*Manihot esculenta*) unmodified and modified with phosphoric acid and citric acid has been successfully employed to remove several heavy metals, such as, chromium, lead, mercury, and zinc (Acosta Arguello et al., 2017; A. Albis et al., 2016; A. R. Albis et al., 2015; Albis Arrieta et al., 2019; Albis Arrieta, Martínez, et al., 2017; Albis Arrieta, Ortiz Toro, et al., 2017; Fonseca et al., 2018).

In this study, cassava peel was evaluated as an adsorbent material for gold recovery. Adsorption capacity of cassava peel was improved through esterification of the functional groups present on the surface of the biomass with citric acid. This is expected to increase the number of active sites and therefore enhance the adsorption performance of the adsorbent. Kinetic and thermodynamics aspects of the adsorption of gold with the modified biomass were assessed.

2. Methodology

2.1 Biomass preparation

Cassava peels (*Manihot esculenta*) were obtained from local suppliers at Baranoa, Atlántico, Colombia. They were manually separated and washed with tap water to remove dirt from its surface. The clean peels were sun dried for 12 hours to evaporate moisture and to eliminate the cyanide precursor compounds. To complete the drying process, the peel was put in an oven at 105 °C for 24 hours. After that, the dried cassava peels were milled to a final size of 200 to 250 µm (Albis Arrieta, Ortiz Toro, et al., 2017).

A second washing was performed using hydrochloric acid 0.1 N for 1 hour, then filtered and washed with deionized water for an additional hour with continuous agitation. Then, it was placed to dry in the oven at a temperature of 90 °C for 24 hours. Finally, it was washed with distilled water in order to remove the remaining acid, repeating the latter three consecutive times with constant agitation, and then drying again in the oven for 24 hours at 90 °C. The washed and dried biomass was stored in an airtight plastic bag and put in desiccator until use (A. Albis et al., 2016).

2.2 Biomass chemical modification with citric acid

Chemical modification with citric acid is described in (A. Albis et al., 2016; Fonseca et al., 2018). Briefly, for each experiment, 3 g of washed and dried cassava peel biomass was mixed with 6 g of citric acid diluted in 20 ml of distilled water (mass ratio biomass: citric acid 1:2); then, the modification reaction was carried out for 3 hours at a temperature of 60 °C using a thermoregulator, with 1% of sulfuric acid as catalyst. Then, the biomass was filtered and placed in the oven at 50 °C for 8 hours, washed with deionized water, and finally, it was dried again in the oven at a temperature of 150° C for 135 minutes (A. Albis et al., 2016).

2.3 Biomass characterization

Proximate and ultimate analysis

Proximate and ultimate analysis were performed on a sample of cassava peel modified with citric acid, according to ASTM D 2243-00: information about the content of ash, volatile matter, residual moisture, calorific power, carbon and hydrogen, sulfur, and nitrogen was obtained.

Point of zero charge

To determine the point of zero charge, several solutions of pH ranging from 3 to 10 were prepared with distilled water and appropriate amounts of 0,1 M HCl and 0,1 M NaOH. These solutions were added to 0,5 g of modified cassava peel and put under agitation on an orbital shaker for 48 hours at room temperature; finally, the final pH was measured (Cristiano et al., 2011).

pH of the adsorbent

The pH analysis of the modified cassava sample was carried out by adding 2 g of the biomass to 100 ml of distilled water and then boiling it for five minutes, then the solution was filtered, and the pH of the solution was measured (Petrov et al., 2000).

Fourier Transform Infrared Spectrometer (FTIR) analysis

To determine the functional groups of the peel surface before and after being modified with citric acid, the analysis was carried out with the Fourier Transform Infrared Light Spectrophotometer (FTIR); in the range of 4000 cm^{-1} to 400 cm^{-1} which is known as medium IR (Girado & Moreno, 2006). 1 mg of the peel was pulverized and weighed for the analysis and mixed with 50 mg of KBr, previously dried for three hours at 110 °C. Finally, a pellet was introduced to obtain the spectra.

2.4 Gold concentration

To measure the gold concentration, the S2 Picofox (Bruker) total reflection X-ray fluorescence spectrometer was used. Once the samples were filtered, the internal standard (10 mg/L of gallium solution (Sigma)) was added, it was vortex for 1 minute and then 5 - 10 µl of the sample was deposited on the quartz sample holder. Sample holders were put on a heating plate until sample dryness, allowed to cool and immediately read in the spectrometer for 5 - 10 min, depending on the expected concentration.

2.5 Evaluation of equilibrium time

For the stock solution preparation, 0,5 g of metallic gold was dissolved in a solution of 8 ml of 0,1 M HNO_3, and the volume was completed with water to a final concentration of 500 mg/L. Adequate amounts of Au stock solution and distillate water were employed to prepare 30 and 300 mg/L Au solutions. To each of these two solutions, 1% of modified biomass was added, and they were brought to a neutral pH 7 at 30 °C. Samples of both solutions were taken at 1, 2, 7, 7,38, 20, 54,6 and 148,4, minutes and analyzed to determinate gold concentration. Obtained results were used to determinate the time of adsorption equilibrium.

2.6 Adsorption isotherms

For the determination of the adsorption isotherms, 10 ml of the selected concentrations of gold were used at the pH and temperature of the test. 1 % of biomass was added and the mixture was stirred at 400 rpm until equilibrium. Subsequently, an aliquot was extracted, filtered and gold concentration was determined using X-ray fluorescence. Adsorption data were fitted to Freundlich, Langmuir, and Temkin models (Araújo et al., 2018).

Freundlich model is described by Eq. 1:

$$\ln q_e = \ln k_f + 1/n \ln C_e \qquad \text{Eq.1}$$

Where q_e and C_e are the equilibrium adsorption capacity and equilibrium concentration, respectively. k_f is related to the adsorption capacity of the adsorbent and n is related to the intensity of adsorption.

The Langmuir model is represented, in its linearized form, by Eq.2:

$$1/q_e = 1/q^b{}_m + 1/C_e \qquad \text{Eq.2}$$

The parameters of the Langmuir model are q_m (the maximum adsorption capacity) and b (the Langmuir parameter).

The Temkin model is described by Eq. 3:

$$q_e=RT/b_T \ \ln K_T+RT/b_T \ \ln C_e \quad \text{Eq.3}$$

Where b_T is related to the heat of adsorption and K_T is the equilibrium binding constant.

2.7 Adsorption kinetics

Adsorption kinetics was evaluated at initial gold concentrations of 10 mg/l and 150 mg/l and three temperatures (25 °C, 35 °C, and 45 °C). pH was fixed at 10 since at this pH was observed the highest adsorption. The methodology was similar to the one used for the determination of the equilibrium time.

The adsorption capacity, *q* (mg Au/g adsorbent), was calculated as (Eq. 4):

$$q= C_0 \, V_0-C_f \, V_f)/m \quad \text{Eq. 4}$$

Where, C_0, is the initial concentration of gold in the solution, C_f is the final gold concentration, V_0 is the initial volume of the solution, V_f is the final volume of the solution, and *m* (g) is the mass of the biosorbent used in the test.

Removal percentage is expressed as (Eq. 5):

$$\% \, \mathit{rem}\text{oval} = (C_0-C_f \ )/C_0 \quad \text{Eq.5}$$

Experimental kinetic data were fitted to the pseudo-second order model (Wu et al., 2009). In its linearized form, the equation of this model is (Eq. 6):

$$t/q_t = \text{l} /K_2 \, q_e^{\,2} + \ 1/q_e \ t \qquad \text{Eq. 6}$$

Where q_e is the adsorption capacity at equilibrium. Values of K_2 were obtained for each experimental temperature. The activation energy of adsorption was obtained from the Arrhenius equation in its linearized form (Eq. 7):

$$lnK_2 = lnA - E_A/RT \quad \text{Eq. 7}$$

3. Results and discussion

3.1 Proximate and ultimate analysis

The results of proximate and ultimate analyzes for no modified and modified cassava peels are shown in table 1. Modified cassava peels have lower content of moisture, ashes, and fixed carbon than the unmodified cassava peels. The lower moisture can be attributed to the final steps of the chemical modification with citric acid where the biomass was dried for several hours. The lower ashes amount could be due a demineralization-like process of the biomass during the acidic conditions of the modification reaction with citric acid and sulfuric acid as catalysts. The higher volatile matter in the modified cassava peel is the result of the modification process that weaken the biopolymers of the biomass and add a small molecule linked by esters bonds, which are weak at high temperatures. The ultimate analysis shows a low sulfur content, which suggests a lesser risk to the environment (A. Albis et al., 2016).

Table 1. Proximate and ultimate of no-modified and chemically modified cassava peels.

	No-modified casssava peel	**Modified casssava peel**
Proximate analysis		
Moisture (%)	14,79	5,03
Ashes (%)	8,39	3,57
Volatile Matter (%)	74,44	80,72
Fixed Carbon (%)	17,17	15,71
Heating Value (Btu/lb)	7346	7619

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	No-modified casssava peel	**Modified casssava peel**
Ultimate analysis		
Carbon (%)	41,83	45,09
Hydrogen (%)	5,8	5,54
Nitrogen (%)	1,12	0,93
Sulfur (%)	0,1	0,06

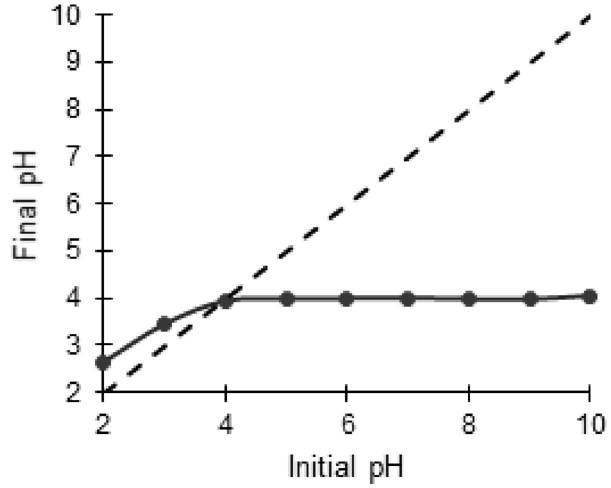
3.2. Point of zero charge

In figure 1 is shown the construct to the determination of the point of zero charge. The curve of final pH vs initial pH intercepts the diagonal in the point of zero charge, PZC = 4.0. At this point, the number of positive charges and negative charges are equal. This value is lower than the PZC = 4,9 reported by (Simate et al., 2015), and the PZC = 5,2 measured by (Jorgetto et al., 2014), probably due to the acidic washing done in our work. The change in the net charge with pH is due to that the functional groups present in the modified cassava peel have different pKa values and, depending on the pH, some functional groups will be positively charged, and others negatively charged. At pHs higher than 4, most of these groups are deprotonated, i.e., they are charged negatively and can attract cations from the solution. Considering that gold is positively charged in solution and above pH 4 adsorbent surface has a net negative charge, a strong attraction is generated between them, and it is expected that gold being adsorbed on the surface of the biomass, i.e., at high pHs the adsorption of gold should improve.

3.3. pH of the adsorbent

The no-modified cassava peel showed a pH of 5,4. In contrast, the pH of the cassava peel modified with citric acid was 2,8. These results suggest that the chemical modification was successful. The lower pH of the modified biomass indicates a higher proportion of acidic sites in the biomass, because of the bonding of citric acid to the biomass surface (A. Albis et al., 2016; Fonseca et al., 2018).

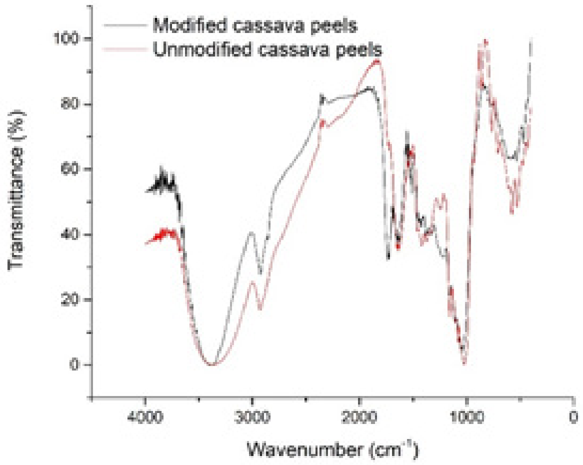
Figure 1. Determination of the point of zero charge



3.4 FTIR analysis

The FTIR spectra for modified and no-modified cassava peels are shown in Figure 2. A wide band is found in the region between 3700 and 3600 cm^{-1} produced by the O-H stretching, which indicates the presence of alcohols and phenols, probably from sugar polymers (cellulose and starch) and lignin, respectively. The main bands in the region from 2000 to 1500 cm^{-1} are due to stretches of double bonds C = C and C = O. The obtained spectra are in concordance with the functional groups of the main components of biomass: cellulose, hemicellulose and lignin, with the presence of some nitrogen containing groups, probably, from some proteins. After modification the intensity of some bands increased: 1739, 1723, 1710, 1707, 1693, 1688 which are related to the C=O stretching of esters and acids and 1226 related with the C-O stretching. This suggests the successful modification of the cassava peels with citric acid.

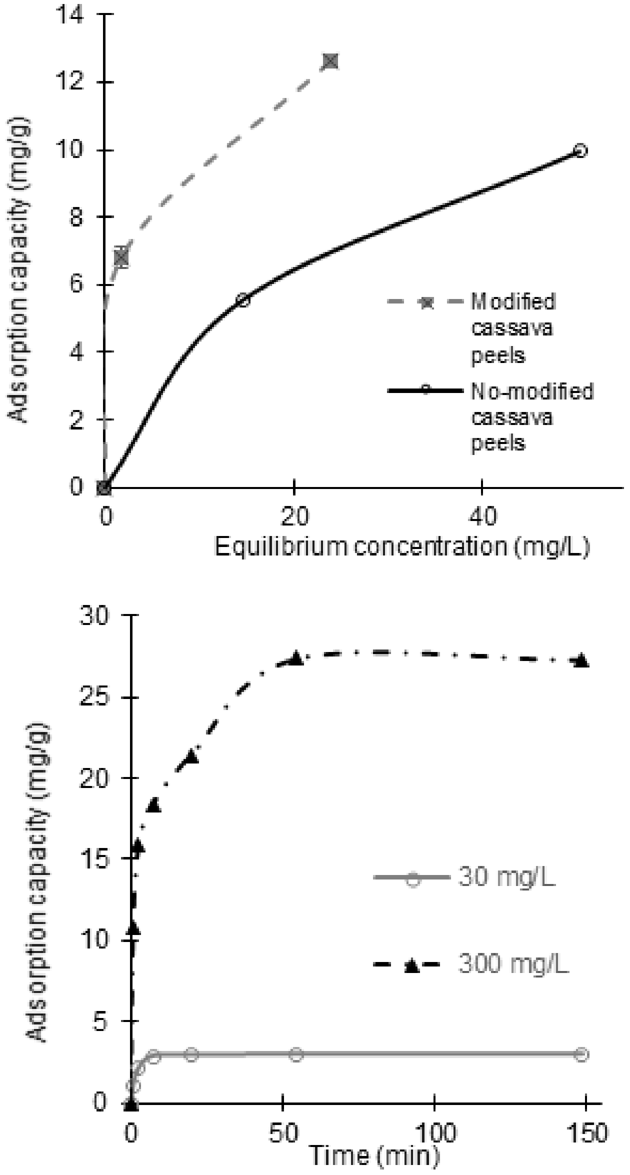
Figure 2. FTIR spectra of modified and unmodified cassava peels.



3.5 Preliminary tests

Preliminary tests were carried out to compare the adsorption performance of the modified and no-modified cassava peels, and to determine the equilibrium time of the adsorption process. Figure 3a compare the adsorption capacity at equilibrium of the modified and no-modified cassava peels. The adsorption capacity, at the same equilibrium concentration, of the modified biomass is almost twice the adsorption capacity of the no-modified peels. This corroborates the successful modification of the adsorbent. Kinetics preliminary tests were carried out at two initial concentrations of gold, as shown in figure 3b. For the gold concentration of 30 mg/l the equilibrium was reached in less than 15 min and the adsorption capacity at equilibrium is 2,8 mg/g. When the initial concentration of gold was increased ten times (300 mg/l), the equilibrium time also increased to about 60 min, and the adsorption capacity at equilibrium was 27,3 mg/g. Similar results were obtained with this adsorbent for other metals (A. Albis et al., 2016; Fonseca et al., 2018).

Figure 3. a) Adsorption capacity for modified and no-modified cassava peels, pH 10, temperature 45 °C, adsorbent dose 1%. b) Adsorption capacity vs time for the adsorption at two initial concentrations of gold using cassava peel modified with citric acid.



Preliminary adsorption kinetic tests, at room temperature, were also carried out using initial concentrations of gold of 30 mg/L and 300 mg/L, as shown in figure 4. To estimate the parameters of the Lagergren equation, the linearized pseudo-second order equation was employed. The adsorptive capacity at the equilibrium (q_e) was estimated as 2,95 mg/g and 27,34 mg/g for initial concentrations of gold of 30 mg/L and 300 mg/L, respectively. The equations of the fitted data are shown in Table 2. The excellent fitting of the experimental data to the pseudo-second order model suggest that the adsorption is not controlled by mass transfer (Tien & Ramarao, 2017).

Figure 4. Kinetic model of pseudo-second order for the adsorption of gold using cassava peels modified with citric acid at initial concentrations of 30 mg/L and 300 mg/L at room temperature, adsorbent doses is 1 %.

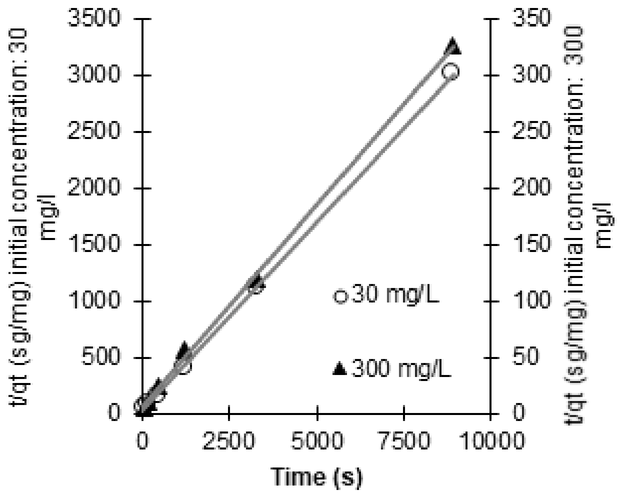


Table 2. Fitting of the kinetic data of the adsorption of gold using cassava peels modified with citric acid to the pseudo-second order adsorption model. q and t units are mg/g and s, respectively.

Initial concentration of gold	30 mg/L	300 mg/L
Pseudo-second order equation	*t/q = 0,3362t + 17,58*	*t/q =0,0358t + 6,3465*
R^2	0,999	0,999

3.6 Thermodynamics of adsorption

Table 3 shows the results of the fitting the equilibrium adsorption data to the adsorption models of Freundlich, Langmuir, and Temkin at several pHs and temperatures. The best fittings were found with the Langmuir model as it can be seen from the values of R^2. The highest percentages of removal were obtained at a pH of 10 and at a temperature of 45 ° C, with an average removal percentage of 95,94% of gold. The lowest adsorption values were obtained at pH 4 and 25 °C with an average removal of 71,86% since this is the point of zero-charge of the adsorbent. In comparison with other biomasses, the percentage of gold adsorption with cassava husk is higher when compared to other adsorbents such as those obtained after the treatment of microorganisms such as bacteria and fungi, specifically gold adsorption studies with Penicillium, Mucor and Gram-negative bacteria obtaining adsorption which showed removals of 96%, 98% and 95%, respectively (Martínez Bautista, 2008).

Table 3. Fitting parameters for the adsorption of gold using cassava peels as adsorbent using Freundlich, Langmuir, and Temkin models.

Freundlich							
pH	**T**	**25 °C**		**35 °C**		**45 °C**	
2	***n***	2,76	2,80	2,38	2,44	2,45	2,41
	k_f*(mg$^{1-1/n}$ l$^{1/n}$/g)*	3,38	3,51	3,61	3,72	4,09	4,01
	R^2	0,79	0,79	0,93	0,92	0,85	0,89
4	***n***	2,66	2,78	4,39	4,39	3,65	3,37
	k_f*(mg$^{1-1/n}$ l$^{1/n}$/g)*	1,42	1,54	2,73	2,88	4,26	3,90
	R^2	0,95	0,93	0,80	0,82	0,65	0,65
7	**n**	2,60	2,29	1,95	2,09	2,70	2,60
	k_f*(mg$^{1-1/n}$ l$^{1/n}$/g)*	3,36	3,02	3,00	3,45	4,68	4,60
	R^2	0,90	0,93	0,94	0,95	0,82	0,90
10	**n**	2,73	3,00	2,52	2,66	2,75	2,64
	k_f*(mg$^{1-1/n}$ l$^{1/n}$/g)*	4,22	5,90	4,27	4,73	5,27	4,84
	R^2	0,82	0,83	0,89	0,83	0,83	0,33

Langmuir							
pH	T	25°C		35°C		45°C	
2	q_m (mg/g)	11,85	11,60	12,64	12,64	12,33	12,59
	b (l/mg)	0,36	0,44	0,46	0,46	0,68	0,61
	R^2	0,97	0,98	0,94	0,94	0,94	0,95
4	q_m (mg/g)	7,76	7,94	8,38	8,67	10,20	10,26
	b (l/mg)	0,09	0,10	0,15	0,16	0,86	0,69
	R^2	0,91	0,91	0,91	0,92	0,95	0,95
7	q_m (mg/g)	12,05	12,42	13,95	13,59	12,55	12,84
	b (l/mg)	0,39	0,33	0,29	0,40	0,87	0,81
	R^2	0,99	0,98	0,96	0,96	0,96	0,97
10	q_m (mg/g)	12,15	12,08	12,89	12,89	12,85	13,32
	b (l/mg)	0,73	0,84	0,68	0,88	1,33	0,85
	R^2	0,99	0,98	0,98	0,98	1,00	0,99
Temkin							
pH	T	25°C		35°C		45°C	
2	At (l/mg)	14,19	16,08	12,67	18,03	16,70	16,09
	b_T (mg J/g mol)	1464	1480	1271	1407	1259	1261
	R^2	0,93	0,95	0,92	0,92	0,90	0,91
4	At (l/mg)	3,08	4,28	81,80	99,05	72,01	40,58
	b_T (mg J/g mol)	1981	2204	3166	3106	1932	1805
	R^2	0,88	0,87	0,77	0,79	0,82	0,81
7	At (l/mg)	13,86	8,03	5,51	8,30	28,94	26,86
	b_T (mg J/g mol)	1435	1264	1029	1099	1349	1332
	R^2	0,96	0,98	0,95	0,95	0,92	0,95
10	At (l/mg)	23,58	41,08	19,47	27,20	39,91	27,17
	b_T (mg J/g mol)	1398	1533	1286	1311	1343	1281
	R^2	0,97	0,96	0,98	0,98	0,99	0,97

The statistical analysis of the maximum adsorption capacity obtained from the Langmuir isotherm is shown in Table 4. The chosen response variable was the maximum adsorption capacity (q_m). The analysis of variance (ANOVA) indicate that pH has a significant effect (95,0% confidence level) on the value of q_m, while the influence of temperature is not significant in the range studied. This suggest that the adsorption of gold on modified cassava peels is robust against temperature changes, but very sensitive to pH.

Table 4. Analysis of Variance

Source	Sum of squares	DF	Middle Square	Reason-F	Value-P
MAIN EFFECTS					
A: Temperature	2,98981	2	1,4949	4,06	0,0768
B: pH	32,2345	3	10,7448	29,17	0,0006
RESIDUALS	2,20976	6	0,36829		
TOTAL (CORRECTED)	37,434	11			

3.7. Kinetic study

The kinetic of the adsorption of gold on modified cassava peels was studied more extensively at pH 10, where maximum adsorption occurs. The measurements were carried out at temperatures in the range of 25 °C to 45 °C and initial concentrations of gold of 10 mg/l and 150 mg/l. The kinetic data was fitted to the pseudo-second order model, as suggested by the preliminary tests previously shown. Kinetic constants for each replicate at the studied temperatures is shown in Table 5. A relatively high dispersion is found for both kinetic constants at low temperature. This could be for a poor temperature control due to the heating produce for the stirring and other devices that is not significant at higher temperatures. Despite these uncertainties at low temperatures, the determination coefficients are higher than 0,95 for the linearized model, and the second order constant shows a clear tendency to decrease with temperature. However, when the experimental q_e values are compared with the obtained with the pseudo-second order model substantial difference are found. These differences arise, probably, because data near equilibrium were not included in the kinetic determination, thus, the obtained kinetic data cannot simulate the kinetic behavior of the adsorption near equilibrium. The parameters obtained could be use in engineering calculations, but only in the range of time in which they were obtained: 15-70 min. A similar observation has been done by (Tien & Ramarao, 2017)and (Tran et al., 2017).

	k_2 (g/mg s)		q_e (mg/g)		q_e Exp (mg/g)	
T (°C)	C_0= 10 mg/l					
25	7,34E-06	1,29E-05	6,17E+00	4,82E+00	9,91E-01	9,94E-01
35	5,24E-05	4,51E-05	2,64E+00	2,80E+00	9,92E-01	9,92E-01
45	4,12E-04	4,07E-04	1,36E+00	1,36E+00	9,95E-01	9,92E-01
	C_0= 150 mg/l					
25	8,12E-07	9,49E-07	6,54E+01	6,10E+01	1,20E+01	1,22E+01
35	4,67E-06	5,50E-06	3,14E+01	3,02E+01	1,26E+01	1,27E+01
45	5,73E-05	6,38E-05	1,56E+01	1,51E+01	1,25E+01	1,28E+01

Figure 5. Arrhenius plot for gold adsorption of cassava peels modified with citric acid. pH 10, adsorbent dose 1 %. Filled circles, initial concentration 10 mg/l; open circles, initial concentration 150 mg/l.

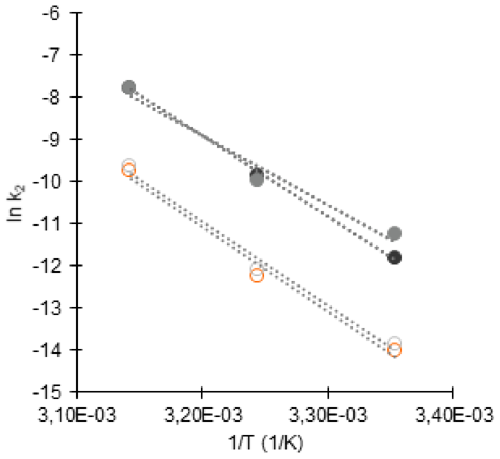


Table 5 shows and excellent fitting to the pseudo-second order model (R^2 close to 1). Figure 5 shows the Arrhenius plot for the obtained kinetic constants. The obtained activation energy is 157 ± 14 kJ/mol. When compared to another gold recovery study (Vargas et al., 2006), the activation energy obtained in this project was very high, which indicates that the reaction needs more energy to occur. This makes sense since the adsorptive capacity for the experiments realized with the temperature of 45 °C was higher than the one obtained with the temperatures of 35 °C and 25 °C.

4. Conclusions

Cassava peels were successfully modified with citric acid as showed by the changes found in FTIR spectra, pH of the adsorbent, and mainly in the absorption capacity of gold. The modified biomass exhibited a higher gold adsorption than the unmodified cassava peels, with removal percentages of up to 99,54%. This percentage of removal is also higher than the reported for other biomasses, such as, fungi and bacteria. On the other hand, the equilibrium time is obtained during the first 70 minutes of the process, and the point of zero charge of the modified cassava peels is around pH 4.

Additionally, the exploration of the pH and temperature behavior of the adsorption of gold on modified cassava peels was carried out. The equilibrium data was best fitted to the Langmuir model. The highest adsorption was obtained at pH 10, but at this pH the temperature had little influence on the maximum adsorption capacity. This was confirmed by the ANOVA, where the temperature did not show significance at the 95% confidence level. This points out to a robust process with low enthalpy of adsorption.

The kinetic model that best represents the gold adsorption process is the pseudo second order, which suggests that this phenomenon is not mass controlled. The obtained activation energy is 157 ± 14 kJ/mol. This high value confirms that gold adsorption on modified cassava peels involve chemical bonds, i.e., it is a chemisorption process.

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