

Evaluation of Zinc Adsorption Using Cassava Peels (*Manihot esculenta*) Modified with Citric Acid

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Abstract

The adsorption of zinc from aqueous solutions on cassava peels (*Manihot esculenta*) modified with citric acid was studied. Cassava peels were modified with citric acid according to a fractional experimental design with central point, which had as independent variables: mixing time, drying time, reaction time, mixing temperature, reaction temperature, and biomass/acid ratio. In order to determine the best conditions to perform the chemical modification, removal experiments were carried out with the samples specified in the experimental design. Under these conditions, kinetic experiments were developed resulting in fast adsorption of zinc with equilibrium times within 20-30 minutes range, and adsorption capacities of 3.042 mg/g and 4.904 mg/g for zinc solutions of 30 and 50 mg/L, respectively. At these initial concentrations of zinc, the experimental data fit the kinetic pseudo-second order model.

Keywords: Adsorption, cassava peels, esterification, Zinc, kinetic models

1 Introduction

Heavy metals present in water and wastewater effluents is one of the greatest challenges of our time because of the physiologic and neurologic damages caused by the exposure to these elements, Therefore, in order to reduce the concentration levels of heavy metals in the environment, a wide range of physical and chemical techniques have been developed to treat wastewater prior to discharge [20]. Classically, methods such as membrane filtration, adsorption, ion exchange, reverse osmosis, chemical precipitation and solvent extraction have been used for heavy metal removal [6]. Zinc has been widely used in industrial applications such as galvanizing, painting, batteries, foundry, fertilizers and pesticides, combustion of fossil fuels, pigment, polymer stabilizers, etc., whereby wastewater from these industries are contaminated with zinc due to its presence in large quantities [6].

Some biomaterials such as castor bean leaves [14], soybean husks [7], sugarcane bagasse [7], orange peels [11], banana peels [4], cassava peels [2], among others, have been widely tested as adsorbents and have shown that they can effectively eliminate heavy metal from wastewater. It has been shown that structural modification by esterification of lignocellulosic materials can improve adsorption kinetics, increase the heavy metal removal percentage and the maximum adsorption capacity. Such chemical has obtained favorable results with sodium hydroxide [3], tartaric acid [23], citric acid [13], among others. In the present study the effect of the variables involved in the esterification of the cassava husk on the percentage of zinc removal was evaluated, furthermore the zinc adsorption kinetics using modified cassava husk were adjusted to the pseudo- first order, pseudo-second order and the intraparticle diffusion model.

2 Materials and Methods

2.1 Reagents

Distilled water, deionized water, and commercial citric acid were used during the pretreatment and modification of cassava peels. Sulfuric acid 96-98%, hydrochloric acid 36-38 %, nitric acid 65%, potassium bromide (KBr), were obtained from MERCK. Furthermore, Zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$), acetone, both from ABC-RD and standard gallium solution (1000 mg/L) from Sigma were used.

2.2 Pretreatment of the adsorbent

Cassava peels were collected in a farm at Juan de Acosta, Atlántico, Colombia. They were rinsed with tap water and exposed to sunlight for 24 hours; then dried at 105 ° C for 24 hours, ground and sieved to a particle diameter between 450 and 250 μm ; washed with a 0.1 M hydrochloric acid solution at 600 rpm for 40 min; finally, rinsed with water to remove the acid, and dried at 50 ° C for 12 hours [11].

2.3 Design of experiments

Monroy *et al.* [16] identified some of the variables with the greatest effect on the adsorption properties of biomass in chemical modification. These variables correspond to the initial concentration of citric acid, the heating time, the temperature of the chemical treatment and the biomass / acid ratio. The levels of experimentation for the chosen variables [7, 13] and the conditions of the design of experiments can be found in Table 1. Statgraphics© was used to design a fractional factorial design 2^{6-2} , and perform the statistical analysis.

Table 1. Experimental factors and levels considered in the design of experiments.

Factor	Level	
	Low	High
Citric acid-biomass mass ratio C:B (g/g)	1.5	2.5
Mixing temperature T_1 (°C)	40	80
Reaction temperature T_2 (°C)	120	180
Drying time (h)	4	12
Mixing time t_1 (h)	2	4
Reaction time t_2 (min)	90	180

2.4 Esterification

The procedure carried out in this study presents some modifications to that used by Marshall, *et al.* [13] and Monroy, *et al.* [16] initially, cassava peels were mixed with citric acid 1.5 to 2.5 grams of citric acid per gram of biomass and 1% by weight of concentrated H_2SO_4 . The mixture was stirred at 500 rpm for periods of 2 to 4 hours at temperatures between 40 °C and 80 °C. Subsequently, the mixture was dried at 50 °C for 4 to 12 hours, washed with 4 to 5 times with deionized water. Finally, the material was heated at temperatures of 120 °C to 180 °C, during periods of 90 to 180 min, according to the experimental design.

2.5 Adsorption tests

Removal adsorption of Zn was performed adding 0.2 g of the modified sample to 20 ml of zinc solution at 30 mg/L. Solution pH was adjusted to either 5 ± 0.3 or 2.8 ± 0.4 , with concentrated NaOH or HCl solution, as necessary. The mixture was stirred at 400 rpm for 30 minutes at room temperature with a magnetic stirrer. The final Zn concentration was measured by X-ray fluorescence (S2 PICOFOX, Bruker). Adsorption capacity (q) was calculated using equation 1 and the percentage of removal (*% of rem*) with equation 2:

$$q = \frac{V(C_0 - C_f)}{m} \quad (1)$$

$$\% \text{ of rem} = \frac{(C_0 - C_f)}{C_0} \quad (2)$$

Where C_0 and C_f are the initial concentration and final concentration of zinc (mg/l), respectively, V is the volume of the solution (l), and m is the mass of the tested adsorbent (g).

2.6 Adsorption kinetics

For the adsorption kinetics analysis, 1 g of modified cassava peels was mixed with 100 ml of zinc solutions at 30 ppm and 50 ppm. The experiments were performed at 25 ° C and 400 rpm. The pH of the solutions was adjusted to pH 5 ± 0.3 using NaOH and samples were taken at 3, 8, 13, 18, 23, 30, 40 and 50 minutes for both assays. The experimental data obtained in the adsorption kinetics analysis were modeled using the linearized form of pseudo-first-order (equation 3) [22], pseudo-second order (equation 4) [8], and the intraparticle diffusion (equation 5) models [21].

$$\ln\left(1 - \frac{q_t}{q_{eq}}\right) = -k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}} \quad (4)$$

$$q_t = k_d t^{1/2} + 1 \quad (5)$$

where, q_t is the amount of adsorbate per mass of adsorbent adsorbed at time t , q_{eq} is its value at equilibrium, k_1 , k_2 , and k_d are the kinetic constants for pseudo-first order, pseudo-second order, and intra-particle models, respectively.

A. Biomass characterization

Infrared spectra were obtained using an IRAffinity 1-S (Shimadzu) spectrometer. The KBr pellet method was employed. Spectra are the average of 100 scans at wavelengths between 4000 cm^{-1} and 400 cm^{-1} with a resolution of 4 cm^{-1} . Proximate and ultimate analyzes for both modified and unmodified samples were carried out according to ASTM D 2243-00.

3 Results and Discussion

3.1 Biomass characterization

Figure 1 shows the FTIR spectra of modified and unmodified cassava peels. Both materials show similar spectra. The band in the range of 3600-3000 cm^{-1} is characteristic of the stretching of the OH bond of cellulose, hemicellulose, lignin, citric acid and H₂O from the residual moisture of the material. The peak observed at 2920 cm^{-1} is characteristic of the stretching of the C-H group. Within the range 1800-1600 cm^{-1} , two peaks can be distinguished corresponding to the stretching of the C=O bond of carboxylic acids and esters; the one around 1750 cm^{-1} is stronger in modified cassava accounting for the successful modification. Finally, the stretch corresponding to C-O bond is located between 1200 and 1000 cm^{-1} , is also stronger

for the modified cassava. Table 2 shows the results of proximate and ultimate analyzes for various lignocellulosic materials together with those analyzed in this work. The unmodified materials are similar in elemental composition although the modified ones present a slight increase in the percentage of carbon, oxygen and a decrease in hydrogen content possibly by the esterification reaction.

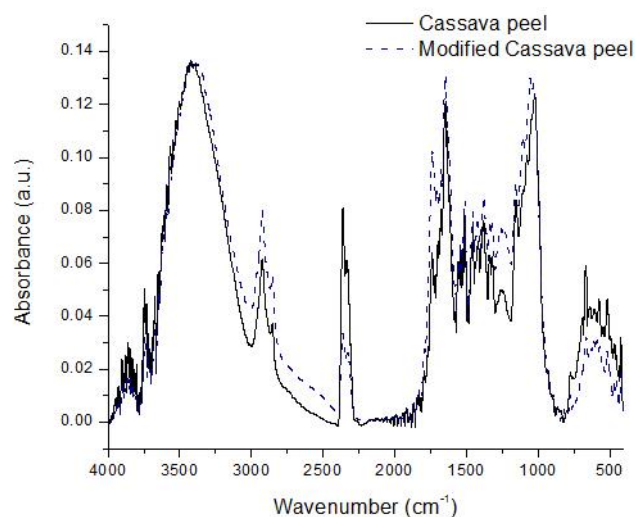


Figure 1. FTIR spectra of unmodified and modified cassava peels.

Table 2. Proximate and ultimate analysis of modified and unmodified cassava peels.

Material	Composition (%)	Unmodified cassava peels	Modified cassava peels	Bamboo [5]	Coconut shell [5]
Ultimate analysis	C	47.21	48.11	44.62	44.69
	H	7.74	5.99	5.54	5.47
	N	1.35	1.22	8.76	9.57
	O	43.70	44.68	41.08	40.27
Proximate analysis	Moisture	7.29	6.17	16.86	12.86
	Ash	1.92	1.15	6.75	7.78
	Volatile	68.16	70.78	63.54	63.76
	Fixed carbon	22.63	21.9	12.85	15.58
	S	0.04	0.18	-	-
	Gross Calorific Value (BTU/lb)	7403	8490	7446.3	7592.4

3.2 Adsorption tests

Adsorption tests were carried out according experimental design at $\text{pH } 2.8 \pm 0.4$ and $\text{pH } 5 \pm 0.3$, of which the latter is considered the optimum pH for zinc removal

according to several authors [1, 11]. In Table 3 is observed the significant increment of the percentage of removal with the increase in about 2 pH units. At pH 5 the maximum percentage of removal obtained was 99.05 %. On the other hand, in the tests carried out at pH 2.8 the maximum percentage of removal found was 68.75 %. The variation in the percentage of removal with pH could be explained by the high concentration of protons at low pH, that makes difficult the cation exchange with the adsorbent [12, 18].

Table 3. Adsorption tests results.

Sample	t ₁ (h)	T ₁ (°C)	Drying time (h)	T ₂ (°C)	t ₂ (min)	C:B ratio	% removal pH 2.8±0.4	% removal pH 5.0±0.3
1	4	40	12	120	90	2.5	57.50	90.19
2	2	40	4	180	90	2.5	21.20	94.33
3	3	60	8	150	135	2.0	35.97	90.93
4	2	40	4	120	90	1.5	38.24	84.30
5	4	80	12	180	180	2.5	50.48	98.17
6	4	80	4	120	90	2.5	12.41	87.49
7	4	40	4	180	180	2.5	28.60	86.68
8	2	80	4	180	180	1.5	26.55	95.11
9	3	60	8	150	135	2.0	39.22	97.38
10	4	40	12	180	90	1.5	18.57	84.18
11	3	60	8	150	135	2.0	68.76	98.95
12	3	60	8	150	135	2.0	64.67	98.45
13	2	40	12	120	180	2.5	23.24	80.09
14	4	80	4	180	90	1.5	41.15	97.29
15	4	80	12	120	180	1.5	47.79	91.83
16	2	80	12	120	90	1.5	6.87	48.51
17	4	40	4	120	180	1.5	66.48	97.19
18	2	80	12	180	90	2.5	23.00	90.82
19	2	40	12	180	180	1.5	4.55	90.11
20	2	80	4	120	180	2.5	15.04	71.24
21	3	60	8	150	135	2.0	67.16	99.05
Unmodified Cassava Peels	-	-	-	-	-	-	39.66	92.66

Statistical analysis of data using Statgraphics[®], shows that the variables with the highest incidence in the percentage of removal, in order of decreasing importance, were: the interaction between the mixing time (t_1) and the reaction temperature (T_2), the reaction temperature (T_2), the interaction between the mixing temperature (T_1) and the reaction temperature (T_2) and finally the mixing time (t_1). The reaction conditions to improve zinc adsorption, according to the statistical analysis, are: citric acid-biomass ratio of 2, 3 hours of reaction at 60 ° C using 1 % of sulfuric acid as catalysts for the first reaction, 8 hours drying, and finally reaction temperature of 150 °C for 135 minutes for the second step. Under these conditions, the average adsorption capacity of the material was 2.92 mg/g and 96.95 % removal, values comparable with the study of Gupta, et al in which an adsorption capacity of 2.4 mg/g and 90-95 % removal using sugarcane bagasse for zinc adsorption [7]. In the assays carried out at pH 2.8 ± 0.4 the modified cassava peels adsorbed 15 % more zinc than the unmodified peels while at pH 5 ± 0.3 adsorbed only 4 % more. This is because the modified material has more active sites than the unmodified one and therefore has more probability to trap heavy metals in environments with high concentration of hydrogen ions.

3.3 Adsorption kinetic

The kinetics of zinc adsorption on the modified cassava peels with the most zinc adsorption capacity was evaluated. Adsorption kinetics was measured for 30 and 50 mg/l zinc solutions. Both solutions reached equilibrium within 20 to 30 minutes. The adsorption capacity at equilibrium was 3.042 mg/g for the 30 mg/l solution and 4.904 mg/g for the 50 mg/l solution, while the removal percentage was 99.29 % and 97.41 %, respectively. Adsorption rate was fast at the start of both experiments and decreased as the contact time increased. This was due to there are a limited number of active sites, so when all sites are available adsorption is fast and then slows down as competition for the remaining active sites intensifies [9].

Figure 2 shows the fitting of experimental data to three kinetics models. In Figure 2A is shown that the fitting of experimental data to pseudo-first order model is poor, with low coefficients of determination, $R^2 = 0.7673$ and $R^2 = 0.8231$, for the solutions with zinc initial concentrations of 30 mg/l and 50 mg/l, respectively. The adjustment of experimental data to the pseudo-second order model (Figure 2B) shows R^2 values close to unity, for both 30 mg/l ($R^2 = 0.9954$) and 50 mg/l ($R^2 = 0.9905$) zinc solutions. The average value of k_2 was $0.076 \text{ g mg}^{-1} \text{ min}^{-1}$. From Figure 2C we can see that data tend to form two straight segments in each curve. According to Singh [21] and Rajic [19] this behavior indicates that diffusion through the pores is not the limiting stage of the adsorption process. Our experimental data fits best the pseudo-second order model suggesting that the dominant phenomenon in the process is chemical adsorption, i.e., adsorption is due to valence forces that involve to share or exchange of electrons between the adsorbent and adsorbate [8].

Table 4 compares the adsorption of zinc on modified cassava shells with other biomaterials. Although, it is not possible to make a very precise comparison it can

be seen that modified cassava peels shows an average adsorption capacity and a very fast adsorption of zinc. This suggests that under appropriate operating conditions, modified cassava shells may be useful in the removal of zinc.

Table 4. Adsorption capacity and kinetics of zinc removal on several adsorbents.

Adsorbent	Zinc Initial concentration (ppm)	Adsorption capacity (mg/g)	pH	% of removal	k_2 (g mg ⁻¹ min ⁻¹)	Equilibrium time (min)	Reference
Mango peels	25	11.83	5.0	67	0.0085	60	[10]
Castor seed hull	50	7.463	5.8	89	0.0038	240	[15]
Castor seed hull	30	5.08	5.8	98	0.0047	240	[15]
Modified cassava peel	50	4.904	4.9	97	0.076	30	This Work
Coffee husks	50	3.7	4.0	79	0.5937	360	[17]

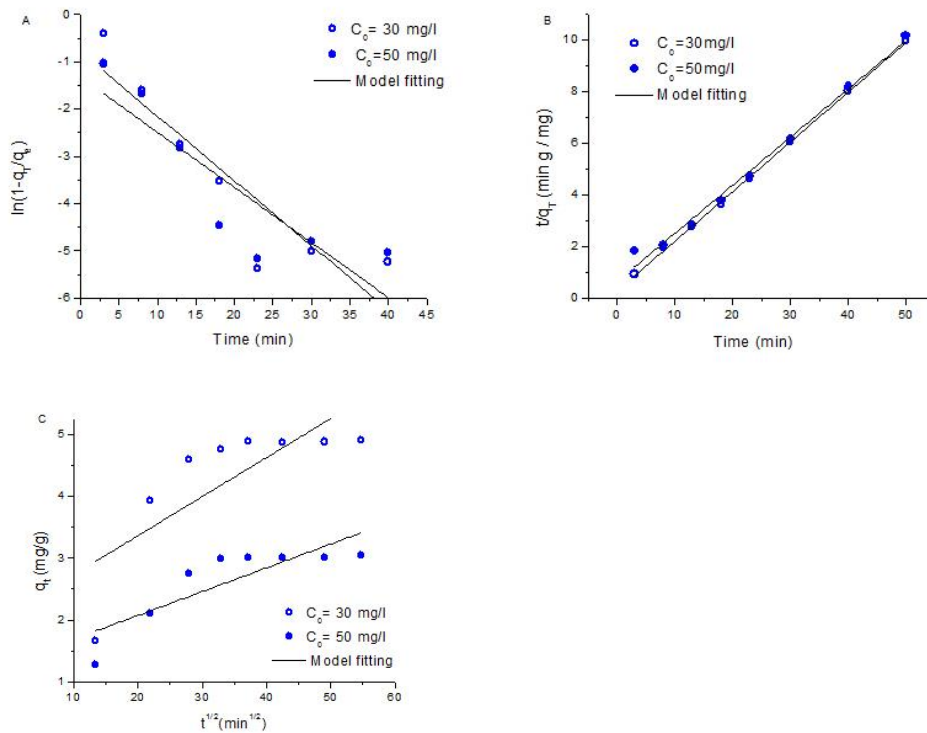


Figure 2. Fitting of experimental data to several kinetics models: (A) Pseudo-first order model; (B) Pseudo-second order model; (C) Intra-particle diffusion model.

4 Conclusions

With the development of this research it was observed that esterification with citric acid allows to increase the amount of active sites of the cassava peels. As a result, the modified material increased the removal percentage and the adsorption capacity compared to the unmodified material. The pH of the solution is one of the variables that most affects the adsorption process with the cassava peels. With the increase of about 2 pH units, 99% zinc removal was achieved. The increase in the initial concentration of solute in the solution increases the adsorption capacity of the material but decreases the percentage of removal. The kinetic study showed that the adsorption of zinc with modified cassava peels is rapid compared to other systems and fits to the pseudo-second order model.

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