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USE OF ORANGE PEELS (*CITRUS SINENSIS WHASHINGTON NAVEL*) FOR OBTAINING PECTIN AS AN ADSORBENT IN THE BIOREMEDIATION OF EFFLUENTS CONTAMINATED WITH LEAD

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Abstract: The orange is one of the most cultivated fruits in Peruvian territory, recording a production of 553,400 tons in 2020. The most commercialized variety is the Washington navel, commonly known as 'huando', where 8.5-9.6% represents the amount of peel generated, a little used byproduct that comprises 6.15% of pectin, a biopolymeric molecule with attractive adsorbent properties. On the other hand, the numerous establishments in Peruvian industrial parks generate effluents contaminated with lead (II) that are discharged into various bodies of water and when entering the food chain, it is harmful to human, animal and plant health due to being a recalcitrant heavy metal.

The work was proposed with the objective of revaluation and use of orange peels, with the extraction and purification of pectin as the main polysaccharide with high adsorbent capacity for the purification of effluents contaminated with lead (II) from industrial establishments.

The extraction of pectin was carried out using the acid hydrolysis method and the evaluation was carried out under Batch adsorption experiments. The determination of the lead (II) concentration was by means of the atomic adsorption spectrophotometry technique, the adsorption mechanism was evaluated by studying the adsorption isotherms and the adsorption kinetics of Pb (II). Of the isotherms evaluated, the investigation was adjusted to the Freundlich isotherm and for the adsorption kinetics the model had a greater adjustment to the pseudo-second order reaction. For a solution of 20 ppm of lead (II), the maximum adsorption capacity was 12,004 mg/g at 4 hours, demonstrating that pectin from orange peel is a useful material as an adsorbent of heavy metals in solution, being the case studied. lead (II).

Keywords: Pectin. Adsorption. Lead. Orange Peels. Isotherms. Kinetics.

INTRODUCTION

Fruits contribute to well-being and food and nutritional security, in addition to improving the standard of living of small farmers dedicated to this activity, generating a positive economic impact for Peru (Pérez et al., 2020).

According to the report from the Ministry of Agrarian Development and Irrigation (MINAGRI), the orange is one of the fruits that contributed the most to the Value of Agricultural Production (VPA) in 2020, with a production of 553.4 thousand tons (MIDAGRI, 2021). However, such production is not free of losses.

In the process of planting and marketing oranges, there are physical and economic losses; Of the physical ones, the detachment and classification operations are considered, while in the economic ones, unforeseen costs are found in the production chain (Pérez et al., 2020). Losses due to seasons and transfers are also considered.

An orange is considered not suitable for marketing if it has cracks, openings and rough skin (creasing), causing losses due to discard. However, its structure does not change, and it can be used in different processes (Berrospi. 2019).

Oranges have three well-differentiated parts (Tsiokano et al., 2021), the flavedo or epicarp, a layer rich in chromoplasts with numerous essential oil sacs (Farag et al., 2020; Tovar et al., 2019) and pigments; the albedo or mesocarp, a layer of white, spongy tissue rich in flavonoids and pectin (Mandalari et al., 2006); The endocarp constitutes the edible part of the fruit, its predominant sugars are glucose, fructose and sucrose.

Due to the large number of components that orange has, it has been used in different areas such as the elimination of metals and toxic oxyanions (Mora et al., 2020), such as chromium (III), copper (II) (Romero- Cano

et al., 2016; Omolara et al., 2021), cadmium (II) (Tran et al., 2016), arsenic (III) (Ortiz. El al, 2023) Selenium (IV) (Mora et al, 2020) and lead (II) (Abdelhafez and Li, 2016; Omolara et al., 2021).

Pectin is a polysaccharide present in the cell wall of several plants, especially fruits, and its main subunit is homogalacturonan and rhamnogalacturonoane-I, which are covalently linked to each other (Ozlem et al., 2024). In food systems it is used as a gelling agent, stabilizer and thickener (Su et al., 2019), on the other hand, it is also widely used as a contaminant adsorbent (Jun Li et al., 2022) due to having a strong affinity for metal ions. Homogalacturonan is a linear domain-like acid α-(1 → 4)-galacturónico pudiendo ser parcialmente metoxilado. Depending on its degree of methoxylation it can be classified as low methoxyl pectin or high methoxyl pectin. The free carboxyl groups present in the acid chain α-(1 → 4)- galacturonic, serve as binding sites and form bonds with heavy metals (Lessa et al., 2017; Wang et al., 2019).

There are several methods for the extraction of pectins such as microwave-assisted extraction (Turan et al., 2024), ultrasound (Patience et al., 2021), enzymes, subcritical water extraction; interesting alternatives to the conventional method, however, these methods usually include some major drawbacks, such as energy-intensive production, high process cost, and the quantity produced is not scalable.

On the other hand, water pollution is critical in Peru, with a variety of contaminants present, with special attention to heavy metals, whose harmful properties, such as their high toxicity, environmental persistence and irreversibility, and their capacity for bioaccumulation in chains. food, raise concern (Nanayakkara et al., 2023). Its origin, both natural and anthropogenic, points to the latter as the main source due to rapid industrial and urban growth (Lintang Nur Fadlillah et al., 2023).

The bioaccumulation of heavy metals occurs when ingestion exceeds metabolization, accumulating in organisms, preceding biomagnification, a process of biological enrichment in food chains (Nanayakkara et al., 2023). This accumulation can cause various health problems in living organisms, such as neurological, cardiovascular, respiratory, gastrointestinal, liver, kidney, and musculoskeletal disorders (El Morabet et al., 2024).

Lead (Pb) is a common toxic metal, even at low concentrations, ranking second on the list of priority toxic substances (Jiong-Li Huang et al., 2024). According to the guidelines given by SUPREME DECREE N°004-2017-MINAM – Peru, the maximum permitted levels of Pb in water that can be made drinkable with disinfection, conventional treatment and advanced treatment is 0.01mg/L, 0.05mg/L and 0.05 mg/L respectively.

The objective of this work was the revaluation and use of orange peels with the extraction and purification of pectin as the main polysaccharide with high adsorbent capacity for the purification of effluents contaminated with lead (II) from industrial establishments.

MATERIALS AND METHODS

PECTIN EXTRACTION

Pectin extraction was carried out using the acid hydrolysis method. Initially, the orange peel was weighed and washed, which was then boiled with distilled water for 10 minutes to inactivate the enzymes present. Subsequently, the solution was cooled and the water was removed. In a separate container, the orange peel was placed in distilled water, adjusting the pH to 3 by controlled addition of hydrochloric acid. The solution was then brought to a boil, filtered to remove residues, and the orange peel was discarded.

The resulting solution was gradually heated until it reached approximately 1/3 of the initial volume, and then cooled. Once the solution reached room temperature, alcohol was added in a proportion of 1 part alcohol for every 3 parts solution. The mixture was left to rest for three hours and then filtered. The gel obtained is identified as pectin and was subjected to a drying process. Finally, the dried pectin was stored in airtight bags for preservation.

PHYSICOCHEMICAL CHARACTERIZATION OF PECTIN

EQUIPMENT AND REAGENTS

The main materials and reagents used to determine the final concentration of the solution included several key elements. These materials include $Pb(NO_3)_2$ solutions, Orange Pectin, Magnetic Stirrer, 0.1N Sulfuric Acid, 0.1N Sodium Hydroxide, pH meter, Analytical Balance, Spectrophotometry Equipment. Each of these components was essential for the experimental procedure and guaranteed the precision of the results obtained.

METHOD

Based on the methodology proposed by Owens et al. 1952, the following tests will be carried out:

FACTORIAL DESIGN

The factorial design used in this study involves the manipulation of three main factors, each with two different levels, and three repetitions. In total, eleven experimental trials were carried out.

Factors: Pb concentration, contact time and adsorbent mass.

Levels: Low and high.

ADSORPTION ISOTHERMS

The adsorption capacity, essential to evaluate the performance of the adsorbent, is quantified using equilibrium isotherms. These isotherms describe the adsorbent-metal ions interaction, commonly applying equations such as the Langmuir and Freundlich models to adjust them. The Langmuir model postulates the formation of a monolayer over the sorption sites during adsorption, while the Freundlich isotherm explains the heterogeneous change in surface energy of the adsorbent.

The analysis of adsorption isotherms, such as Langmuir and Freundlich, provides crucial data to understand the adsorption mechanism, being essential in the efficient design of adsorption systems and contributing to the development of sustainable technologies.

For the study, the Langmuir and Freundlich isotherms were evaluated, for this we worked with 4 different concentrations of $Pb(NO_3)_2$ each of 20 ppm, 15 ppm, 10 ppm and 5 ppm in 1L of distilled water, adjusting to a pH of 5 with 0.1N H_2SO_4 or 0.1N NaOH; Then 0.5 g of orange pectin was added to each one. The solutions were placed on a magnetic stirrer for a time of 1 h, 2 h, 3 h, 4 h and with constant stirring of 200 rpm.

Finally, the four samples were carefully subjected and analyzed by spectrophotometry, a precise method, for determining the final concentration of the solution.

ADSORPTION KINETICS

The adsorption process involves both surface adsorption and diffusion in the pores, aspects examined through the application of specific kinetic models. Among them the pseudo first order and pseudo second order kinetic model. These tools were used in the study of the adsorption process of pectin adsorbents for heavy metal ions. This approach allows a deeper and more complete

Physicochemical characterization	Equation
Determination of humidity and solids	$\%\ Humidity = \frac{Mass\ of\ original\ sample\ (g) - Mass\ of\ dry\ sample\ (g)}{Mass\ of\ original\ sample\ (g)}\ x\ 100\ \%$
Determination of ashes	$\%\ Ashes\ = \frac{(Crucible\ Weight\ with\ Ashes\ -\ Crucible\ Weight\ Only)}{Sample\ weight}\ x\ 100\ \%$
Determination of equivalent weight	$Equivalent\ weight = \frac{Sample\ weight\ (mg)}{meq\ of\ NaOH}$
Determination of free acidity	$free\ acidity\ = \frac{meq\ of\ NaOH}{g\ acid\ component}$
Esterification degree	$\%\ ES\ = \frac{meq\ of\ NaOH\ (methoxyl\ cont.)}{meq.of\ NaOH\ (free\ acidity) + meq.of\ NaOH\ (methoxyl\ cont.)} x\ 100\%$
Degree of methoxylation	$\%Methoxyl\ = \frac{meq\ of\ NaOH\ x\ MW\ of\ Methoxyl\ x\ 100}{Sample\ weight\ (mg)}$
Determination of Galacturonic Anhydride Acid (GAA)	$\%GAA\ = \frac{meq\ of\ NaOH\ x\ MW\ of\ Methoxyl\ x\ 100}{Sample\ weight\ (mg)}$

Table 1.- Equations to carry out the physicochemical characterization.

[a]Methods used at western regional research laboratory for extraction and análisis of pectic materials (Owens et al. 1952)

	Langmuir model	Freundlich model
Definition	It is generally accepted for chemisorption and for physical adsorption at low pressures and moderately high temperatures.	It shows an empirical relationship that allows us to accurately determine the adsorption capacity; it is only applied to low and intermediate concentration ranges.
General Equation	$\frac{C_e}{q_e} = \frac{1}{QK} + \frac{C_e}{Q}$	$q = KC_e^{(1/n)}$
Where:	q_e Amount of adsorbate retained depending on the initial concentration.	
	Q Maximum amount of adsorbate retained per 1g of adsorbent.	
	Ce Adsorbate concentration when the adsorption system reaches the state of thermodynamic equilibrium.	
	K Adsorption capacity constant.	
	n It is the adsorption intensity constant. (n > 1: physical adsorption), (n < 1: chemical adsorption)	

Table 2.- Adsorption isotherms (Langmuir and Freundlich)

[a]Preparation, characterization, and adsorption kinetics of graphene oxide/chitosan/carboxymethyl cellulose composites for the removal of environmentally relevant toxic metals (Rahman et al., 2024)

	Pseudo First Order Model	Pseudo Second Order Model
General Equation	$q_t = q_{eq}(1 - e^{-k_1 t})$	$q_t = q_{eq}\left(1 - \frac{1}{q_{eq}k_2 t + 1}\right)$
For the graph	$log(q_{eq} - q_t) = log(q_{eq}) - \frac{k_1 t}{2.803}$	$\frac{t}{q_t} = \frac{1}{q_{eq}{}^2 k_2} + \frac{1}{q_{eq}} t$
Where:	q_{eq} Amount of solute adsorbed at equilibrium per unit mass of adsorbent, ($mg.g^{-1}$).	
	q_t Amount of solute adsorbed at equilibrium per unit mass of adsorbent at time *t*, (mg. g).$^{-1}$	
	k_1: Pseudo-first order rate constant, (min).$^{-1}$	
	k_2: Pseudo second order rate constant, (g/mg/min).	
	t: Adsorption time	

Table 3.- First and second order kinetics

[a]Preparation, characterization, and adsorption kinetics of graphene oxide/chitosan/carboxymethyl cellulose composites for the removal of environmentally relevant toxic metals. (Rahman et al., 2024)

understanding of the variation in the metal concentration distribution in the adsorbate-adsorbent phases as a function of time, temperature and constant pressure.

This kinetic analysis is crucial to determine the adsorption rate and understand the underlying mechanism behind the adsorption process.

To study the adsorption kinetics, the pseudo first order and pseudo second order models were evaluated and we worked with a concentration of 20 ppm in which four 1 L solutions of lead nitrate were prepared and the pH was adjusted to 5 with H_2SO_4 0.1N or NaOH 0.1N, as appropriate; Afterwards, 0.5g of orange pectin is added to each one and subsequently stirred constantly at 200 rpm for a constant time of 4 hours.

Finally, the four samples were analyzed by spectrophotometry to determine the final concentration of the solution.

RESULTS AND DISCUSSIONS

PHYSICOCHEMICAL ANALYSIS OF PECTIN

Pectins are divided into two categories based on their level of methoxylation: low methoxyl pectin, with less than 50% methoxylation, and high methoxyl pectin, with more than 50%. Non-methoxylated galacturonic acid residues can be ionized, allowing pectin to bind metal ions.

Apart from the degree of methoxylation, it has been observed that the distribution of methoxylation also influences the adsorption of pectin by heavy metals. According to research, a lower degree of methoxylation and a higher amount of successive demethoxylated galacturonic acid in homogalacturonan lead to more Pb(II) cross-linked pectin chains, which contributes to the formation of stiffer gels.

According to the physicochemical analysis of pectin (Table 4), a low degree of methoxyls can be observed with a value of 39.31% less than 50%, which makes it suitable for the adsorption of heavy metals.

Parameters	Sample to treatment	Units
Humidity	39,34	%
Solids	60,66	%
Ashes	1,18	%
Equivalent Weight	144,93	mg/meq
Free Acidity	6,90	meq/g
Methoxyls	39,31	%
Esterification	64,76	%
AAG	35,18	%

Table 4.- Physicochemical analysis of pectin

According to the bibliography consulted, it has been highlighted that the adsorption capacity of pectin is favored when Ca^{+2} is used. However, in the context of the present research, this component was not used. Therefore, it is considered pertinent to make the following recommendation.

FACTORIAL DESIGN

Table 5 shows the results of lead adsorption in the different proposed tests.

According to the results presented in Table 5, it is observed that tests 2 and 6 exhibit the lowest adsorbance, while test 9 demonstrates the highest adsorption capacity, reaching a removal percentage of 59.5%. These findings are significant for the study, highlighting a contact time of 3 hours and an amount of 0.4 grams of orange pectin as the most representative values for the research.

ADSORPTION ISOTHERMS

The Langmuir Isotherm postulates that there are uniform adsorption energies at the surface and that the adsorbate does not move along the surface. The Freundlich isotherm, an empirical tool, is used to represent heterogeneous systems. This equation suggests that the absorption energy in an adsorbent

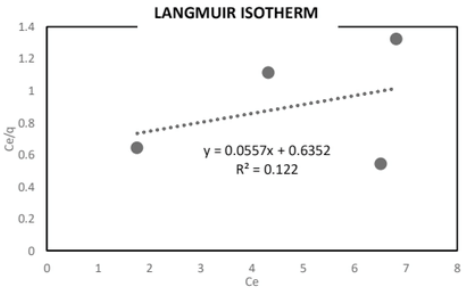
Sample Numbr	Solution volume (L)	[Pb $(NO_3)_2$]	pH	Temperature (°C)	Adsorbent mass (g)	Time (h)	[Initial Pb] (ppm)	[Pb] final (ppm)	[Pb] adsorbed	% Pb(II) removal
1	1	20	5	25	0,50	4	12,51	6,51	6,00	47,97
2	1	20	5	25	0,50	2	12,51	8,67	3,84	30,70
3	1	20	5	25	0,30	4	12,51	7,80	4,71	37,66
4	1	20	5	25	0,30	2	12,51	8,45	4,06	32,46
5	1	10	5	25	0,50	4	6,26	4,21	2,05	32,70
6	1	10	5	25	0,50	2	6,26	4,32	1,94	30,94
7	1	10	5	25	0,30	4	6,26	2,60	3,66	58,44
8	1	10	5	25	0,30	2	6,26	2,98	3,28	52,36
9	1	15	5	25	0,40	3	9,38	3,80	5,58	59,50
10	1	15	5	25	0,40	3	9,38	3,83	5,55	59,18
11	1	15	5	25	0,40	3	9,38	3,81	5,57	59,40

Table 5.- Adsorption results

Initial [Pb] (ppm)	Adsorbent mass (g)	Contact time	Final concentration (ppm)	% removal of Pb (II)	Removal Capacity (mg/g)
12,51	0,5	4	6,51	47,97	12,0042
9,38	0,5	3	6,81	27,43	5,1481
6,26	0,5	2	4,32	30,94	3,8800
3,13	0,5	1	1,76	43,73	2,736

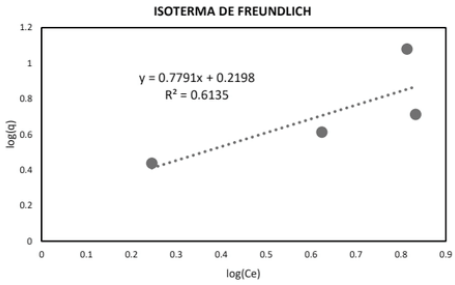
Table 6.- Final concentration of Pb(II)

varies depending on whether the adsorption sites are previously occupied.



Graph 1.- Langmuir isotherm

Interpretation: Using the graph we calculate the value of R2 to identify the relationship of the variables, a value close to one demonstrates the representativeness of the isotherm



Graph 2.- Freundlich isotherm

Interpretation: Using the graph we calculate the value of R2 to identify the relationship of the variables, a value close to one demonstrates the representativeness of the isotherm

Langmuir isotherm			Freundlich isotherm		
Q(mg/g)	K(L/mg)	R²	K($mg^{1-1/n}g^{-1}L^{1/n}$)	n	R²
17,5439	0,0936	0,122	1,6588	1,2835	0,6135

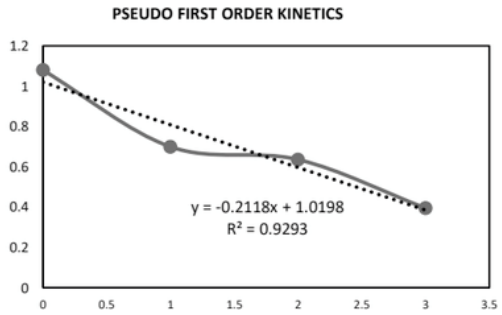
Table 7.- Adsorption isotherm data

The Freundlich isotherm is the one that fits the empirical data, so it describes phenomena in physical adsorption which involves the

Van Der Walls forces, a multi-molecular adsorption is proposed, forming multilayers on the surface of the adsorbent, this is due to the increase in the adsorbate concentration.

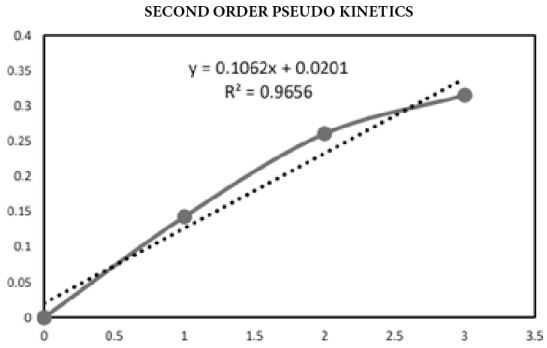
The constant "n" indicates the intensity of the adsorption capacity and "k" is the equilibrium constant that indicates where the isotherm cuts on the ordinate axis. The higher the value these constants reach, the greater the adsorption capacity of pectin.

ADSORPTION KINETICS



Graph 3.- Pseudo first order kinetics

Interpretation: Effect of the amount of lead adsorbed per unit mass of adsorbent with respect to time, for a single concentration of lead and mass, at a constant temperature.



Graph 4.- Pseudo second order kinetics

Interpretation: Effect of the amount of lead adsorbed per unit mass of adsorbent with respect to time, for a single concentration of lead and mass, at a constant temperature

Pseudo first order			Pseudo second order		
Qmax	K1	R2	Qmax	K2	R2
12,004	-0,5937	0,9293	49,751	0,003804	0,9656

Table 8.- Adsorption kinetics

According to the graphs, the contact time necessary to reach equilibrium conditions is 4 hours.

The kinetic curves show the variation of the adsorption capacity with time (qt). For an initial concentration of 12.5 ppm of Pl^{+2}, the maximum adsorption capacity is 12.004 mg/g. The correlation coefficient indicates that the predominant model is the second order, predicting with greater accuracy the values of the adsorption capacity over time.

CONCLUSIONS

The pectin from orange peel is a good adsorbent of heavy metals, the case study being lead (II), this is due to the ability to form a bond between the carboxyl group of the α-(1 → 4)- galacturonic and metals.

From the treatment of the experimental data it was concluded that the adsorption phenomenon is physical (physisorption) and forms multilayers on the surface of the adsorbent, therefore the Freundlich isotherm model was used with which the maximum biosorption capacity of 12, 0012 mg/g which corresponds to a removal percentage of 47.97%

The equilibrium time was reached after 4 hours of stirring. The best fit of the kinetic results was obtained with the pseudo-second order model with high correlation values (R2>0.97) in all cases, which would imply that the kinetics are not affected by the different established parameters.

Experience shows that the orange considered as waste or loss can be used, giving a new application and added value to its components, such as the pectin present in its peel.

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