

UNIVERSIDAD SAN FRANCISCO DE QUITO USFQ

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**Comparative study of commercial adsorbent walnut shell
with residual biomass for the removal of organic
compounds present in produced water**

Ensayo o artículo académico

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RESUMEN

Se realizó el estudio de la eficacia de la adsorción de compuestos orgánicos en agua producida con diferentes fuentes de biomasa residual. Los análisis de adsorción se realizaron con cuesco de palma, cáscara de naranja, cáscara de plátano, cáscara de maracuyá, pepas de cacao y aserrín, para comparar su capacidad con respecto al adsorbente comercial, cáscara de nuez. Todos los adsorbentes se sometieron a un simple proceso de tratamiento, antes de la adsorción, que consiste en un lavado, un secado y una etapa térmica. Los análisis de adsorción utilizando agua producida sintética mostraron que únicamente el cuesco de palma y el serrín adsorben los compuestos orgánicos del agua sintética, expresado como la concentración de la demanda química de oxígeno (DQO), en el procedimiento experimental por lotes. Se consideraron tres modelos de isotermas: Langmuir, Freundlich y Temkin. Entre estos tres modelos, Langmuir describe mejor los datos experimentales para la cáscara de nuez, cuesco de palma y serrín. Se determinó la capacidad máxima de adsorción. Así, el serrín presentó un valor máximo de 33 mg / g, mientras que la cáscara de nuez y el cuesco de palma presentaron una capacidad de 4,9 mg / g y 5,6 mg / g, respectivamente. Los resultados de la cinética de adsorción se describen mejor mediante la ley potencial de pseudo-primer orden en los experimentos llevados a cabo con la cáscara de nuez y cuesco de palma. Los experimentos del punto de ruptura indican que el cuesco de palma se saturará antes que la cáscara de nuez.

Palabras clave: adsorción; biomateriales; agua producida; cáscara de nuez; biomasa residual; cinética de adsorción; isoterma; ruptura de adsorbente; filtración

ABSTRACT

The effectiveness of the adsorption of organic compounds in produced water with different residual biomass sources was studied. Adsorption analysis were made with palm shell, orange peel, banana peel, passion fruit peel, cacao bean and sawdust to compare their capacity with respect to the commercial adsorbent walnut shell. All adsorbents undergo a simple pretreatment process, prior to the adsorption, consisting of a washing, drying and a thermal step. The adsorption analyses with synthetic produced water show that only palm shell and sawdust actually adsorb the organic compounds in the synthetic water, expressed as the concentration of chemical oxygen demand (COD) in the batch experimental procedure. Three isotherm models were considered: Langmuir, Freundlich and Temkin. Among these three models, Langmuir best described the experimental data for walnut shell, palm shell and sawdust. The maximum adsorption capacity was determined and sawdust presented a maximum value of 33 mg/g while walnut shell and palm shell presented 4.9 mg/g and 5.6 mg/g, respectively. Kinetics results were best described by pseudo-first order potential law in the experiments carried out with the walnut shell and palm shell. Breakthrough experimentation shows that palm shell will saturate earlier than walnut shell.

Keywords: adsorption; biomaterials; produced water; walnut shell; residual biomass; adsorption kinetics; isotherm; adsorbent breakthrough; filtration

Comparative study of commercial adsorbent walnut shell with residual biomass for the removal of organic compounds present in produced water

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Abstract

The effectiveness of the adsorption of organic compounds in produced water with different residual biomass sources was studied. Adsorption analysis were made with palm shell, orange peel, banana peel, passion fruit peel, cacao bean and sawdust to compare their capacity with respect to the commercial adsorbent walnut shell. All adsorbents undergo a simple pretreatment process, prior to the adsorption, consisting of a washing, drying and a thermal step. The adsorption analyses with synthetic produced water show that only palm shell and sawdust actually adsorb the organic compounds in the synthetic water, expressed as the concentration of chemical oxygen demand (COD) in the batch experimental procedure. Three isotherm models were considered: Langmuir, Freundlich and Temkin. Among these three models, Langmuir best described the experimental data for walnut shell, palm shell and sawdust. The maximum adsorption capacity was determined and sawdust presented a maximum value of 33 mg/g while walnut shell and palm shell presented 4.9 mg/g and 5.6 mg/g, respectively. Kinetics results were best described by pseudo-first order potential law in the experiments carried out with the walnut shell and palm shell. Breakthrough experimentation show that palm shell will saturate earlier than walnut shell.

Keywords: adsorption; produced water; walnut shell; residual biomass; adsorption kinetics; isotherm; adsorbent breakthrough

1. Introduction

The oil and gas production tend to generate large quantities of contaminated water known as produced water. This water is composed of formation water, the water naturally present in the reservoir, and injection water, that could have been previously injected in the reservoir [1]. Both formation and injection water eventually rise to the surface and are extracted at the wellhead along with gas and oil. Due to the large amount of contaminants in the produced water, this cannot be discharged directly into the ocean or reinjected back into the well [2]. Therefore, a treatment is required. The volume of water needed for injection, depends on the type of deposit and its production mechanism. In most countries legal regulations for injecting wells are increasingly stringent to protect fresh water aquifers [3]. For this reason, it is necessary to develop new water treatment technologies, which will reduce the difficulties in the

bottom of the wells for injecting or for the disposal of produced water [4]. Finding the most appropriate technology for water treatment production depends on several factors, such as disposal methods, environmental impact and of course the economic investment [5]. As oil extraction rises the amount of reinjected water increases considerably, in order to maintain the underground reservoir pressure. Because of the great importance of not wasting water resources, water treatment for reinjection has become crucial for oil-producing companies [6]. The produced water treatment is mainly based on a sequence of steps according to the oil and solids amount presented in the water. The first stage is characterized by the separation of hydrocarbons by flotation units. In order to achieve maximum purity in the first stage, a process of highly effective filtration is employed. Filters based on organic substrates are particularly suitable for this application, ensuring the

elimination of up to 98% of contaminants in the feed water [7].

Worldwide, 140 million metric tons of biomass are generated each year by agricultural activities. This volume of biomass can be converted into an enormous amount of energy and raw material [8]. Filtration processes using adsorption have drawn attention from various industries. The main advantages of filtration using organic substrates include the use of large amounts of residual biomass, which leads to obtaining low cost raw materials, high efficiency for contaminant removal and minimizing the use of chemical or biological products [9, 10]. In this project, the biomaterials were used to determine its potential in removing organic compounds present in produced water by analyzing the equilibrium adsorption isotherm and the kinetics.

2. Materials and methods

2.1. Substrate selection, pretreatment and characterization

Walnut shell (WS), palm shell (PS), orange peel (OP), banana peel (BP), passion fruit peel (PP), cocoa beans (CB), and sawdust (SD) were used as adsorbents for organic compounds in produced water. WS is the commercial product, which was obtained from AF Hidrotecnologia, a company that imports and implants this kind of adsorbent for water treatment. WS was already shredded and had a particle size between 0.3-1.18 mm, which was used to select the particle size of the other adsorbents. PS was collected from a local center of palm oil extraction. OP, BP and PP were collected from a local fruit plantation. The biomaterials obtained locally were shredded and sieved so it can be select a particle size between 0.3-0.6 mm. The pretreatment consisted of soaking and washing the adsorbents with distilled water until no dust is shown, and oven drying at 100°C for 24 h to constant weight. Only in the case of the PS an additional pretreatment was performed by heating it at 180°C for 8 h. In the case of OP, BP, PP and CB, the pretreatment time was 3 h, because dry curves were analyzed and this was the optimum.

Residual biomasses used as adsorbents in this study were characterized so it can be compared with the commercial adsorbent WS. The characterization was first carried out by determining the WS solid gradation so the particle size for the other biomaterials can be selected. The amount of water

present in PS, OP, BP, PP, CB and SD was measured by following the ASTM E1756, where a dry sample is obtained in a Thermo/Precision Scientific 25EM oven. Using the residuals in the humidity experiments, the amount of ashes and total volatile organic compounds were determined by the calcination of the dry samples in a Thermolyne 48000 furnace heated to 550°C for 8h. The bulk density and real density were also measured for all the biomaterials, as well the space between particles and uniformity coefficient.

2.2. Produced water characterization and preparation of synthetic produced water

The contamination in produced water was measured by the chemical oxygen demand (COD) which shows the amount of degradable material present in a sample [11]. To obtain the COD value the water sample was diluted with H₂SO₄ 98% and a potassium dichromate solution as the Manganese III Digestion Method, U.S. Patent 5,556,787 indicates. The sample were digested using a DRB 200 preheated to 150°C for 2 h, so it can be measured in a HACH DR 890 colorimeter. The composition of produced water was also analyzed by a Shimadzu gas chromatograph mass spectrometer (GCMS) QP-2010-Ultra.

The COD of the water sample was 1300 mg L⁻¹. The results obtained by the GCMS analysis showed that produced water has compounds with large and lineal carbon chains with carboxylic functional groups. For the preparation of the synthetic produced water (SPW), gasoline, oleic acid and car oil were used in proportions that presented a similar COD value to the collected produced water. The contaminants were mixed with distilled water for 1 h and then, using a sedimentation funnel, the mixture was left to rest for 1 h.

2.3. Experimental setup for batch adsorption

The experimental setup were carried out by mixing 4g of adsorbent with 40.0mL of SPW with a known concentration. Because of SD density, the batch experiments using this adsorbent were carried out using 0.2g/40.0mL of SPW. The adsorption processes generally are affected by the adsorbent dosage. To obtain the maximum adsorption capacity it is necessary to determine the optimum dosage of adsorbent. When analyzing the effect of adsorbent dosages, an idea of the amount of contaminants that could be adsorbed using the minimum amount of

adsorbent can be considered. In general, as the amount of substrate increases, the amount of contaminants removed increases as well [12].

In this study the adsorbent used for experimentation was WS. With the maximum value of WS dosage, PS, OP, BP, PP, and CB dosage were selected. The effect of amount of adsorbent was studied, ranging dosages from 0 to 10g/40.0mL of 1300mg L⁻¹ SPW. Also, The effect of the contact time was determine by agitating the mixtures for different times between 1 to 120 min, and then filtering the mixture so COD can be measure. The Langmuir, Freundlich and Temkin isotherm models were used to describe the adsorption process. Pseudo first order and pseudo second order were used to determine the adsorption kinetic mechanisms. The experiments were triplicated so the results were obtained as an average.

2.4. Filtration system design and breakthrough experimentation

In order to set a good comparison between the commercial and the best residual biomass adsorbent, it is necessary to understand and explain the saturation time for the materials used [13]. The breakthrough curves for the adsorbents that had a comparable percentage removal were obtained. This experimentation was settled in a laboratory packed bed filtration system with downward flow and shown in Fig. 1.

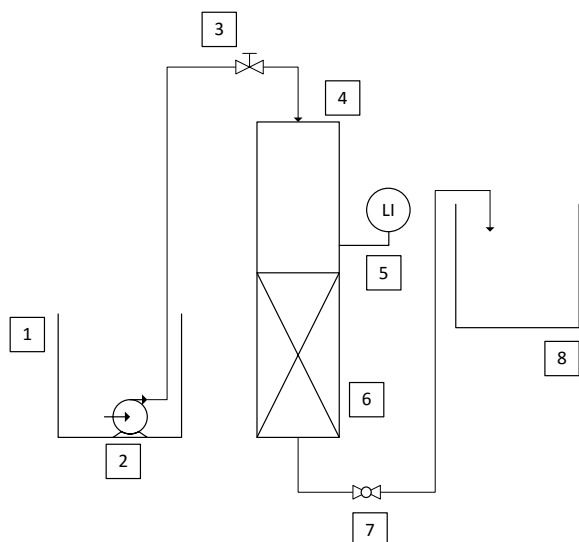


Fig. 1 Packed bed filtration system. (1) Feed water storage tank; (2) submersible pump; (3) feed control valve; (4) column; (5) liquid level indicator; (6) fixed bed; (7) exit valve; (8) sample collection

The determination of the breakthrough curves was carried out as a continuous experimentation by determining a residential time for the SPW in the filtration system. Adsorbent packed bed occupied 50% of the filter. Experimentation was performed working with a pressure drop at the exit, so channeling could be avoided. Samples of treated water were collected every minute for an hour. COD of the samples were analyzed and the breakthrough time for the adsorbents were determined.

3. Theory

3.1. Adsorption capacity

In order to understand the batch experimentation it is necessary to obtain the biomaterials' adsorption capacity. The amount of organic contaminants adsorbed per gram of adsorbent was calculated from the following equation [14]

$$q_t = (C_0 - C_e)V/m \quad (1)$$

Where q_t : adsorption capacity at time t (mg/g of adsorbent), C_0 : initial concentration of contaminants in SPW (mg/L), C_e : equilibrium concentration of contaminants in SPW (mg/L), m : dry weight of adsorbent (g), V : volume of SPW (L).

The percentage of removal of the contaminants present in SPW was calculated using the following equation [15].

$$\% \text{ Removal} = (C_0 - C_e)100/C_0 \quad (2)$$

3.2. Adsorption isotherms

To understand the adsorption process, isotherm models need to be described. An isotherm is a term used to describe the equilibrium curves in an adsorption process [16]. When talking about predictive modeling for design and analysis of adsorption systems, the equilibrium isotherms have a significant role. The experimental data obtained in a specific study may fit under one set of conditions, ergo an isotherm model, but fail under a different one [17]. In this study three isotherm models were considered: Langmuir, Freundlich and Temkin. Table 1 shows the non-linear and linear equation for the models mentioned. In all models the dependence of the q_e , equilibrium adsorption capacity (mg/g of adsorbent) is given by a relation with de contaminant concentration at equilibrium, C_e (mg/L). On the other hand, each model considers different parameters to explain the behavior of the adsorption process.

The Langmuir adsorption model is the most common model used to quantify the amount of adsorbate in an adsorbent as a function of the partial pressure or the concentration at a given temperature [17, 18]. This model assumes that the adsorbent is in contact with a solution that contains adsorbate attracted to the surface and that the surface possesses a specific number of active sites where the molecules of solute can be adsorbed [19, 20]. Thus, this model assumes that the adsorption occurs over a homogenous adsorbent surface and a monolayer coverage of adsorbate takes place [17]. To understand the equations given in Table 1 for the Langmuir isotherm model it is necessary to explain the parameters that are considered. The maximum adsorption capacity, q_m (mg/g adsorbent) and the Langmuir constant, b_0 (L/mg) are related to q_e and C_e .

The Freundlich isotherm model is given by an empirical equation, which can be used when the adsorption involves systems with heterogeneous surfaces, where there is no adsorption limited levels [21, 22]. This model relates the solute concentration

present in the adsorbent surface, with the solute concentration present in the liquid in contact [23]. The parameters related to the q_e for this case are: the substrate adsorption capacity, k (mg/g(L/mg)^{1/n}); and the heterogeneity factor, n . The heterogeneity factor obtained is a measure of the adsorption intensity or the surface heterogeneity. When the value of the slope gets near zero, it means that the process is more heterogeneous [24].

Because of the adsorption heat interaction, the Temkin isotherm model is considered. This model assumes that the energy of the molecular adsorption is characterized by a uniform distribution of the bond energies [25]. This means that the heat of adsorption of the molecules present in the surface layer would decrease with the coverage in a linear way [20]. The discussed isotherm considers: the ideal gases constant (J/mol K), R ; the temperature at which adsorption takes place, T (K); Temkin constant related to the adsorption heat, b_t (J/mol) and Temkin isotherm constant, k_t (L/g) [26].

Table 1
Isotherm models equations

Isotherm	Equation	Linearized equation	Plot
Langmuir	$q_e = \frac{q_m b_0 C_e}{1 + b_0 C_e}$	$\frac{C_e}{q_e} = \frac{1}{b_0 q_m} + \frac{1}{q_m} C_e$	$\frac{C_e}{q_e}$ vs C_e
Freundlich	$q_e = K_f C_e^{1/n}$	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$	$\ln q_e$ vs $\ln C_e$
Temkin	$q_e = \frac{RT}{b_T} \ln(K_T C_e)$	$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e$	q_e vs $\ln C_e$

Table 2
Kinetic models equations

Kinetic model	Equation	Linearized equation	Plot
Pseudo-first order	$\frac{dq_t}{dt} = K(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t)$ vs t
Pseudo-second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{1}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e}$	$\frac{1}{q_t}$ vs t

3.3. Adsorption kinetics

In order to understand the mechanism of adsorption and the possible rate-determining step, including mass transport and chemical reaction, kinetics models are analyzed. In this study the models that are used to understand the adsorption of organic compounds with residual biomass are the pseudo-first order and pseudo-second order, the non-linear and linear equations that describes these models are illustrated in Table 2. Where k_1 and k_2 are the kinetic constants for each model.

The non-linear equations for both models can be linearized by integration, where the boundary conditions are $q_t = 0$ in $t = 0$ and $q_t = q_t$ in $t = t$. In the case of the pseudo-first order equation, the constant k_1 and the value of the adsorption capacity in equilibrium, q_e are obtained by plotting $\ln(q_e - q_t)$ vs t . On the other hand, the pseudo-second order model is based on the adsorption of solid phases [16]. A plot t/q_t versus t gives a line from which the constant k_2 and q_e can be obtained.

4. Results and discussion

4.1. Characterization of the substrates

So it can be determine the proper substrate for the removal of organic compounds, it is necessary to know the properties of each material. A summary of the parameters considered for the characterization are show in Table 3 Humidity is a very relevant

parameter, since the solid with higher humidity will need more time to get saturated with water and so start adsorbing. Also, the organic total solids (oTS) show the organic compounds that are already present in the biomaterial. Substrates with higher amounts of oTS will probably give information about the adsorption capacity, since the substrate will get saturated faster. For this reason, all materials with high oTS percentages will need an additional pretreatment in order to reduce the amount of oils and organic compounds that are already presented in the substrates. Fig. 2 compares basic composition of the different biomass. In Table 3, also bulk density and real density are presented, as well as uniformity coefficient.

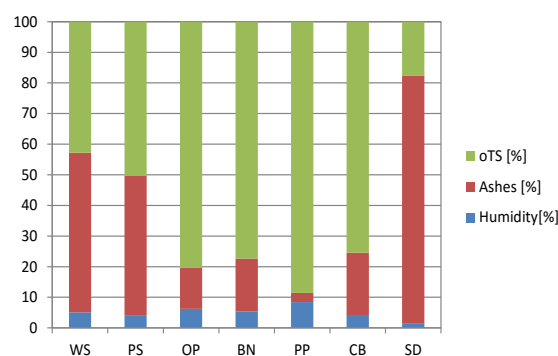


Fig. 2. oTS, ashes and humidity values for different substrat

Table 3.
Substrates Characterization

		WS	PS	OP	BP	PP	CB	SD
Humidity	[%]	5.113	3.987	6.231	5.332	8.453	4.245	1.354
Ashes	[%]	52.119	45.779	13.427	17.323	2.984	20.319	81.079
oTS	[%]	42.768	50.234	80.342	77.345	88.563	75.436	17.567
Real density	[g/mL]	0.698	0.754	0.709	0.632	0.453	0.509	0.018
Bulk density	[g/mL]	0.875	0.899	0.854	0.785	0.653	0.621	0.045
Uniformity coefficient	[-]	1.75	1.82	1.732	3.713	1.345	2.843	1.872
Particle size	[mm]	0.3-1.18	0.3-0.6	0.3-0.6	0.3-0.6	0.3-0.6	0.3-0.6	0.3-0.6

WS: Walnut shell, PS: Palm shell, OP: Orange peel, BP: Banana peel, PP: Passion fruit peel, CB: Cacao beans, SD: sawdust

4.2. Experimental Setup using walnut shell

The effect of WS dosage is shown in Fig. 3. As expected, the percentage of removal tends to increase while the dosage of adsorbent is higher. The maximum adsorption capacity is reached when the dosage of WS is 6.0g with a 60% of removal at the initial concentration of 400 mg/L. Therefore, the dosage defined for the batch experimentation was 4.0g/40mL of SPW, so it can have an adsorbent-water relation of 1:10. In the case of the SD, the amount of adsorbent used was of 0.2g/40 mL of SPW since the density of SD is too low.

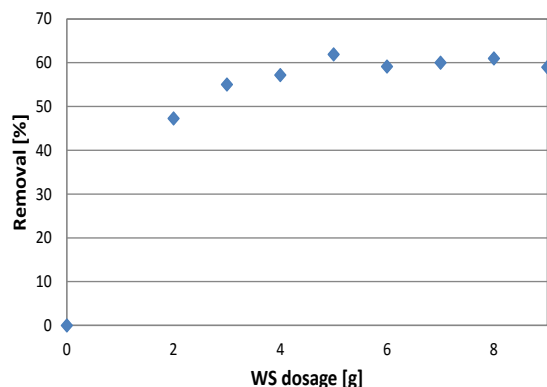


Fig. 3 Effect of WS dosage at room temperature

It is important to analyze the effect of contact time, given that this is a parameter that provides information on how fast is the adsorption process is going. Fig. 4 shows the effect of contact time for the removal of contaminants in SPW by WS. It can be observed that equilibrium was reached within 10 min of agitation, but it is not quite clear, which means that the experimentation needs to be executed for a larger period of time and higher initial concentrations need to be used. The problem lies in the properties of the adsorbent, when WS was put through experimentation, with higher contact times, it could be observed that the particles started to be shredded by the agitation affecting the water COD analysis as shown. Effect of contact time ranging the initial concentration was analyzed with a maximum agitation time of 10min, results are shown in Fig. 5.

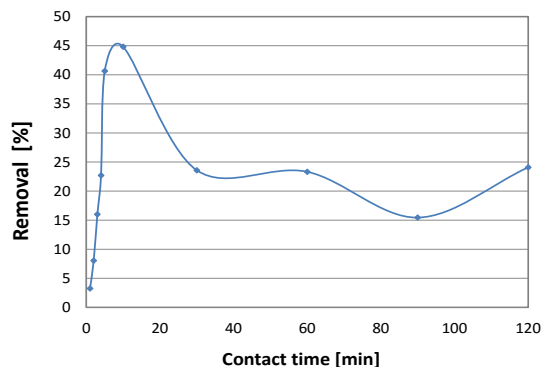


Fig. 4 Percentage removal according to contact time. 4g of WS, 40ml of SPW

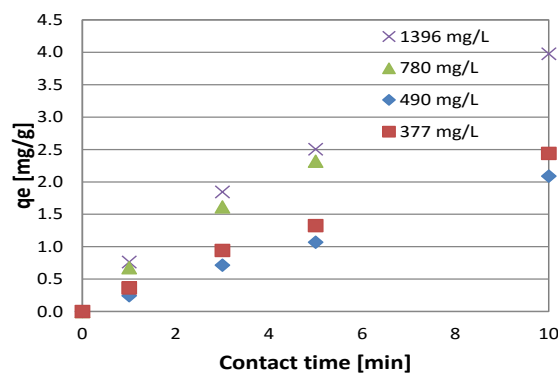


Fig. 5 Effect of contact time using WS as adsorbent

Effect of initial concentration was also analyzed. WS batch experimentation was performed ranging the initial contaminant concentration between 1396–377 mg/L. As Fig. 6 shows, the percentage removal tends to increase when the initial concentration is lower. The maximum percentage removal using WS is 55%.

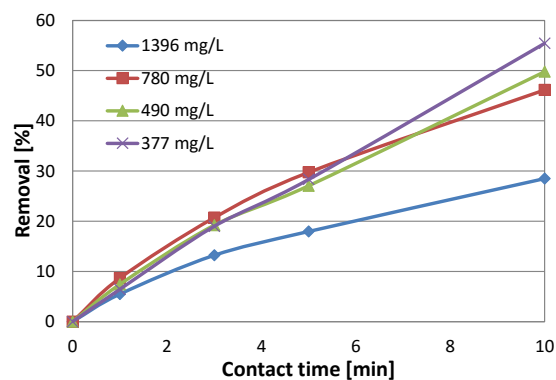


Fig. 6 Effect of the initial concentration in percentage removal using WS, dosage 4g

Produced water salt content was considered too, since it can interfere with the substrates' adsorption capacity. According to Izquierdo et al [30], a common salinity concentration in produced water is 55000 mg/L NaCl equivalent. All salinity studies were accomplished using WS and varying initial salt concentration within the reported value, as can be seen in Table 4.

Table 4.
Salinity studies with 1432 mg/L initial COD

NaCl [g/L]	0.00	30.00	40.00	50.00	60.00	70.00
COD [mg/L]	998.00	1001.33	1063.67	999.33	1026.00	1041.00

After the analysis were made, the substrate did not present any change in its surface. According to the COD values presented in Table 4, it can be said that salt content in produced water does not affect adsorption for this study. Yet, more analysis should be made increasing salt concentration in order to verify its relevance in the adsorption process.

4.3 Comparison of adsorption capacity of different residual biomass

For the adsorption analysis, the optimal adsorbent dosage was used. COD was measured from samples taken after 1, 3, 5 and 10 minutes of contact time. Unfortunately, OP, BP, PP, and CB were unable to adsorb. Due to the large amounts of soluble compounds, such as tannins, coloring agents, sugars and resins present in the biomass, the produced water had a greater COD after adsorption [29] as it is shown in Table 5. Thus, produced water was more contaminated rather than purified. For this reason, the following analysis were performed only with WS, PS and SD.

Table 5
Adsorption analysis for all substrates at an optimal contact time (5 min)

COD[mg/L]	WS	PS	SD	OP	BP	PP	CB
initial	377.00	488.00	445.00	464.00	464.00	464.00	464.00
final	243.33	350.35	342.51	1122.23	1072.54	993.53	1024.68

As it is indicated in Table 5, the COD for WS, PS and SD decreases after adsorption. However, as it was stated before, the COD for OP, BP, PP and CB increases considerably after adsorption, because the mentioned components are solubilized in the produced water altering its color and pollution grade. Following analysis were carry out using only WS, PS and SD.

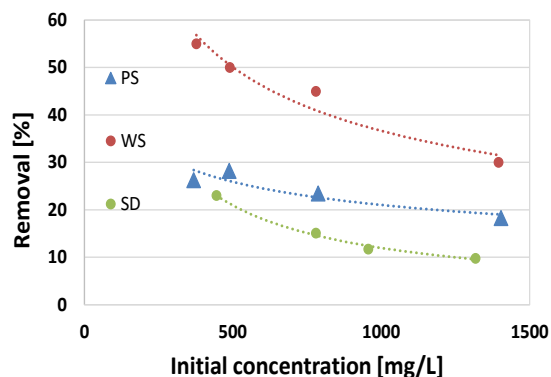


Fig. 7. Effect initial concentration on the percentage removal using WS, PS and SD.

The effect of initial concentration using PS and SD was also studied, so the results obtained for WS can be compared. The removal percentage decreases as the initial concentration increases. WS, PS and SD initial concentration experimentation results are shown in Fig. 7. This figure reveals that the amount of organic compounds adsorbed per unit of mass increases as the initial concentration increases from 300 to 1400 mg/L. When the initial concentration of contaminant increases, the maximum adsorption capacity increases too because of a rise in the mass transference due to higher contaminants concentration [28].

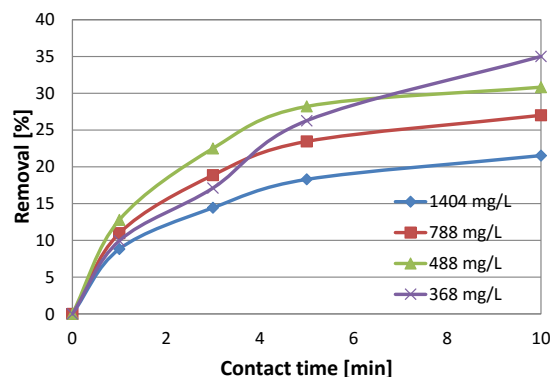


Fig. 8. Effect of the initial concentration in percentage removal using PS dosage 4g

The highest removal obtained using WS as adsorbent was 55%. On the other hand, the lowest removal was 25% obtained in the experimentation with the SD. Nevertheless, these results do not give any information regarding the maximum adsorption capacity. In Fig. 8 Fig. 9 is shown the percentage of removal calculated at different times, ranging the contaminant initial concentration. As can be

observed, PS presents higher percentage removal than WS. However, WS presented the highest removal.

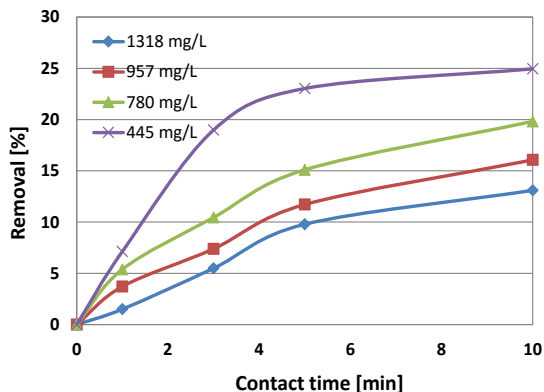


Fig. 9. Effect of the initial concentration in percentage removal using SW dosage 0.2g

Fig. 10 displays the effect of contact time for the removal of contaminants in SPW by PS. This time the equilibrium is reached when the initial concentration is 1400 mg/L, this value is higher than the concentration used when working with WS. In both cases it was observed that a fast adsorption of contaminants occurred. When working with lower initial concentration of contaminants, during the first 5 min the percentage removal was approximately 50% for WS and 35% for PS. On the other hand, the effect of contact time experimentation using SD showed that the maximum percentage of removal was 25% and a similar behavior was present, as Fig. 11 shows.

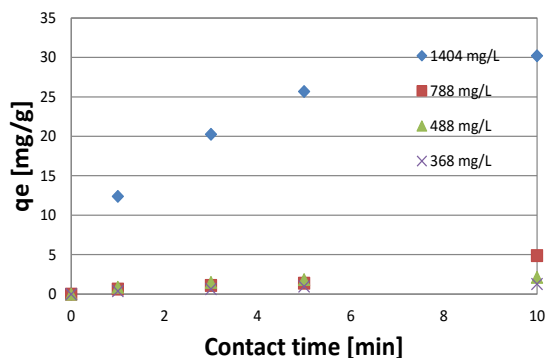


Fig. 10. Effect of contact time using PS as adsorbent

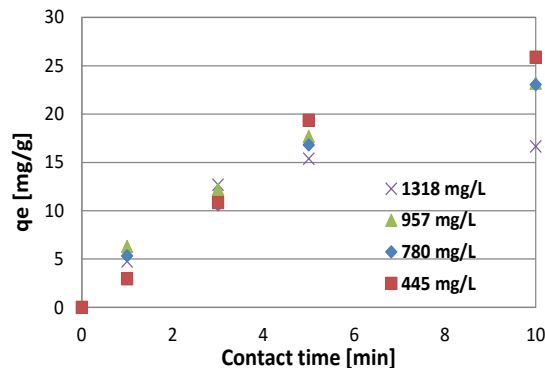


Fig. 11. Effect of contact time using DS as adsorbent

4.4. Adsorption Isotherms Modelling

The coefficients and constants of each isotherms were obtained from the slope and intersection of the linear plots of each isotherms, all the values are shown in Table 6. After Comparing the R^2 of each plot, we can determine that Langmuir best describes the experimental data for walnut shell, palm shell and sawdust. Therefore, the adsorption takes place in a monolayer, in specific homogenous sites, this way, no more than one molecule can occupy a specific site. Hence, no further adsorption can be accomplished. As can be seen in Table 6, the maximum adsorption capacity (q_m) for walnut shell is 5.0384 g / g, for palm shell it is 4.9240 g / g and for sawdust it is 32.7869 g/g. With These results, sawdust presented the best characteristics for adsorption. However, its very low density can affect the filtration since it could cause channeling. Finally, the nonlinear isotherms for WS, PS and SD were drawn and shown in Fig. 12, Fig. 13 and Fig. 14 respectively.

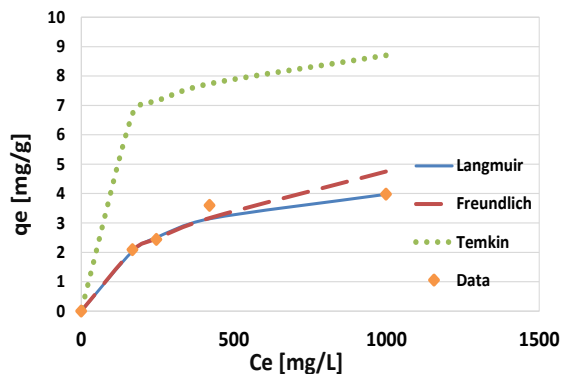


Fig. 12. WS Nonlinear Isotherm

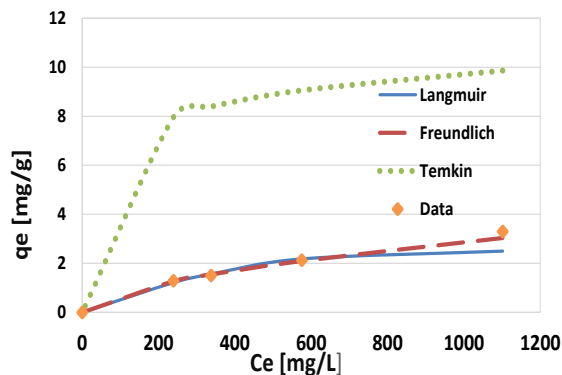


Fig. 13. PS Nonlinear Isotherm

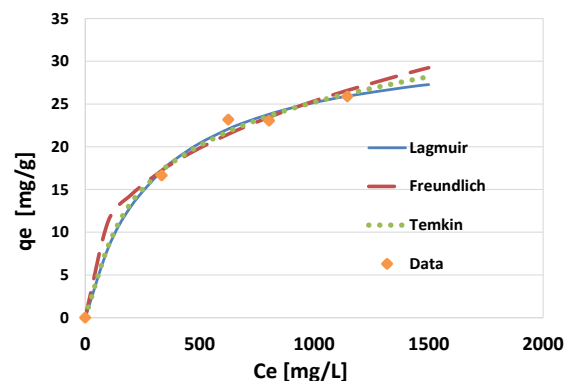


Fig. 14. SD Nonlinear Isotherm

Table 6.
Isotherms relevant coefficients

Langmuir		Freundlich			Temkin			
WS								
b_0	0.0013	L/mg	K_f	0.0561	$(\text{mg/g})(\text{L/g})^{1/n}$	b_t	20.779	J/mol
q_m	5.6380	mg/gS	$1/n$	0.5700	-	K_t	2.372	L/g
R^2	0.9861	-	R^2	0.9972	-	R^2	0.9851	-
PS								
b_0	0.0042	L/mg	K_f	0.1870	$(\text{mg/g})(\text{L/g})^{1/n}$	b_t	21.5760	J/mol
q_m	4.9240	mg/gS	$1/n$	0.4690	-	K_t	2.4520	L/g
R^2	0.9994	-	R^2	0.8680	-	R^2	0.9956	-
SD								
b_0	0.0033	L/mg	K_f	2.2129	$(\text{mg/g})(\text{L/g})^{1/n}$	b_t	7.3192	J/mol
q_m	32.7869	mg/gS	$1/n$	2.8329	-	K_t	0.0313	L/g
R^2	0.9896	-	R^2	0.9265	-	R^2	0.9416	-

4.5. Kinetics studies

The models previously mentioned are fitted to the experimental data by linear regression analysis. Batch experiments were carried out to obtain the effect of contact time and kinetics information. The pseudo-second order rate expression was first used with the experimental data from the WS and PS experiments. Nevertheless, for this model there was

no fitting by any of the adsorbents used as shown in Fig. 16. On the other hand, pseudo-first order model was also applied to the experimental data. In both cases as shown in Table 7 the R^2 is near 1 for all the variation in the initial concentration. The fitting of the data is shown in Fig. 15. The kinetics constants are shown in Table 7.

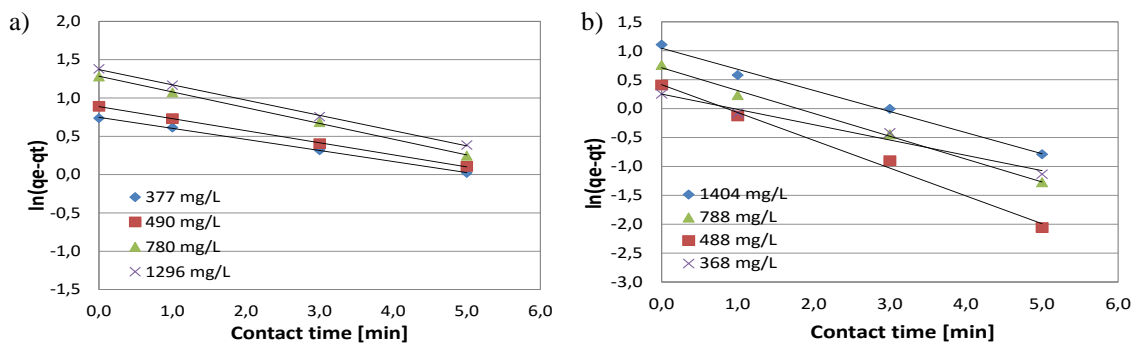


Fig. 15 Pseudo-first order modeling for a) WS b) PS

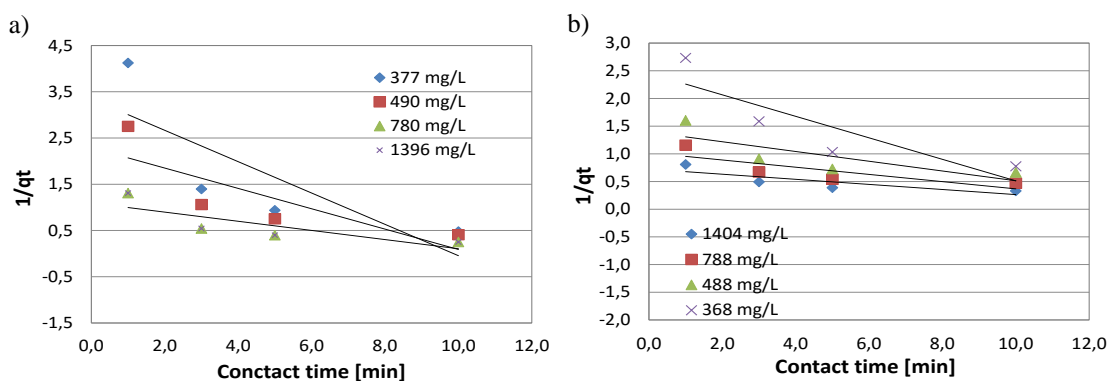


Fig. 16 Pseudo-second order modeling for a) WS b) PS

Table 7
Kinetics constants

Adsorbent	PS				WS			
	1404	788	488	368	1296	780	490	377
Pseudo-first order								
q_e (mg g ⁻¹)	2.8417	2.0269	1.5110	1.2843	3.9385	3.6103	2.4298	2.1111
k_1	0.3652	0.3952	0.4808	0.2647	0.1991	0.2054	0.1573	0.1442
R^2	0.9919	0.9959	0.9930	0.9773	0.9992	0.9995	0.9993	0.9992
Pseudo-second order								
q_e (mg g ⁻¹)	-21.7391	-11.3636	-5.1493	-15.3609	-2.9515	-4.5475	-10.0908	-10.0908
k_2	0.0029	0.0270	0.0017	0.0076	0.0343	0.0211	0.0089	0.0089
R^2	0.6985	0.6208	0.7458	0.6600	0.6616	0.6616	0.6671	0.6392

4.6. Breakthrough Curves

To understand which adsorbent presents better qualities for the removal of contaminants in produced water, it is important to determine how long the adsorbent is going to work at its full capacity. The

breakthrough curves were obtained for WS and PS. SD was not considered for this experimentation because of its density. As it can be observed, Fig. 17 shows the obtained breakthrough curves for WS and PS. It was expected that the saturation time for PS was going to be lower than WS. Because the

maximum adsorption capacity of PS is higher, the saturation point is going to be reached faster. For WS the breakthrough of the material starts at 15min, while for PS starts at 8min approximately

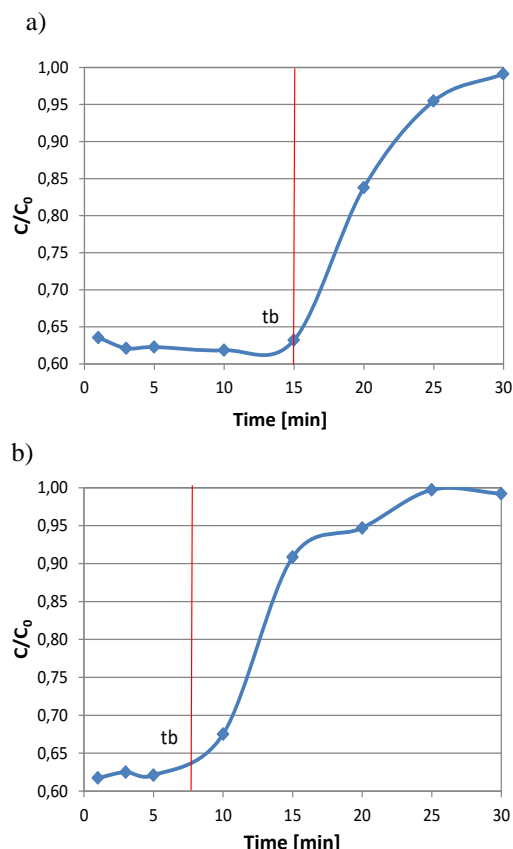


Fig. 17 Breakthrough curves for a) WS and b) PS

5. Conclusions

This study showed that residual biomass adsorption is an effective method for the removal of organic compounds present in produced water. The results obtained with the adsorption analysis show that even though residual biomasses are good adsorbents, not all of them can be used without a pretreatment. Because of this, orange peel, banana peel, passion fruit peel and cocoa beans were not able to perform a good adsorption in this study. Some studies have shown that these substrates are capable of adsorbing organic compounds, as long as an activation method is used, such as heat or acid contribution. The batch experimentation for the adsorption isotherms modeling suggests that all models presented a good fitting for contaminants adsorption with walnut shell, palm shell and sawdust. Langmuir was the model which best describe the

experimental data in these cases. The maximum adsorption capacity was determined and sawdust had the highest value. However, this material has very low density which can cause several problems in the filtration process. Also, kinetics models were performed, and the results showed that both walnut shell and palm shell are better described by a pseudo-first order reactions. With these parameters, a more substantial study could be carried out, including the regeneration process of the biomass. Breakthrough curves showed that palm shell can saturate faster than walnut shell. Breakthrough experimentation was not performed using sawdust because of its density.

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