

Adsorption of paraquat on activated carbon from oil palm shells

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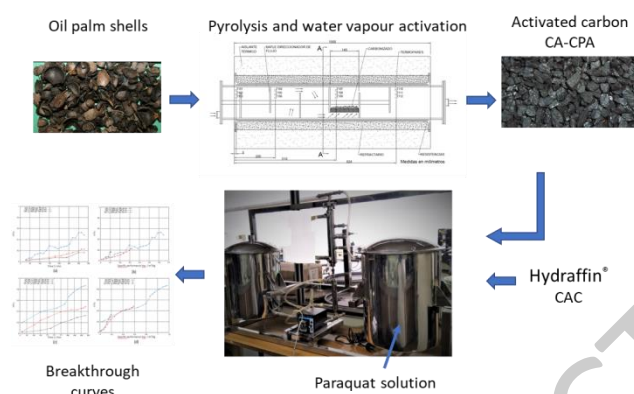
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Graphical abstract



Abstract

Oil Palm Kernel Shell (OPKS) is a residue of the palm oil extraction process, which has good characteristics for the production of activated carbon (AC). Colombia ranks fourth in the world in palm oil production and it is estimated that in 2019 the amount produced of OPKS was approximately 336000 ton per year. Within the contaminants of surface waters, the pesticide paraquat is identified as one of the most dangerous for human health and is at the same time one of the most used in agriculture in Colombia. It is found worldwide in natural waters in the range of 50 µg/l to 5000 µg/l. Oil palm kernel shells were first carbonized in a horizontal oven under N₂ atmosphere until 850 °C for 30 min. After that, three batches, each of 300 g of the carbonized OPKS (COPKS) were activated in the same horizontal reactor by means of partial gasification using H₂O as reaction agent. The activation process starts with a heating stage by raising the temperature from 20 °C to 850 °C in approximately 280 minutes under a N₂ atmosphere. Then in the activation stage the flow of N₂ is replaced by a flow of 20,68 l/min steam while maintaining the temperature at 850 ± 10 °C for another 310 minutes. Finally, the flow of steam is changed to N₂ and the oven is cooled down until ambient temperature. As a result of the activation process, an activated carbon (AC-CAC) with approximately 50 % degree of activation and a surface area of 1200 m²/g

were obtained. The adsorption capacity of the AC-CAC towards paraquat is studied by measuring breakthrough curves in an adsorption column using initial concentrations of paraquat between 600 µg/l and 5000 µg/l. A comparison is performed by using a commercial activated carbon CAC from the company Donau Carbon ref. Hydraffin®. The determination of the concentration of paraquat in water is made by voltammetry.

Keywords: Paraquat, adsorption, activated carbon, oil palm shells, breakthrough curves

1. Introduction

In the world there are 35 million km³ of fresh water of which man can use from 9,000 to 14,000 km³ and currently 5,950 km³ are used. The distribution of the water together with demographic growth constitute a supply problem for some regions (FAO, 2013; ONU, 2017; De Schutter, 2009; FAO, 2013). The worrying environmental situation due to the polluted waters coming from the agroindustry makes research on ways to remove contaminants a priority of greatest impact on the ecosystem and human health (FAO, 2002). Among the most used pollutants in the agricultural sector worldwide is paraquat pesticide (EPA, 2019; EPA, 2018; FAO, 2002). In Colombia it is marketed under the name of Gramoxone and is widely used as an herbicide in coffee, banana, rice, tomato, cocoa, citrus, cotton, cane, potato, corn, beans, lettuce and sorghum among others (ICA, 2017). This herbicide has a toxicity risk level I. In the United States it is of restricted use or application by certified personnel, while in the European Union it is included among hazardous substances for production, import and export, which led to some member states withdraw or suspend it. In Colombia it is found in the table of registered pesticides of the Ministry of Agriculture (W.H.Organization, 2010; EPA, 2019; European, 2011; Minagriculturam, 2020). In the country there is evidence of contamination of freshwater bodies that could be used as drinking water, as in the case of Ventaquemada in the Department of Boyacá where paraquat in concentrations above the permitted limits with concentrations of 600 g/l were found. The maximum permitted limit of paraquat in drinking water for both Colombia and for the United

States is 200 g/l (MINSALUD, 1998; EPA, 2018; Alza-Camacho *et al.*, 2016).

To generate options regarding the removal of contaminants from water and specifically of the pesticide paraquat, the different pesticide removal technologies are considered and at the same time the necessary raw material. Activated carbon has been studied to removal of pesticides and specifically of paraquat, determining adsorption isotherms and concluding that good results are obtained (Hamadi *et al.*, 2004; Foo and Hameed, 2010; Bansal and Goyal, 2005; Sieliechi and Thue, 2015).

Colombia is the fourth palm oil production worldwide producer, with a share of 2 % after Thailand with 3 %, Malaysia with 32 % and Indonesia with 53 %. In 2015 Colombia produced 1273000 ton of crude palm oil that were obtained from 5937000 ton of processed palm fruit and it is estimated that the amount of oil palm shells generated was 300000 ton. In 2018 the production of fresh palm fruit was 7531000 tons with a quantity 376550 tons of oil palm shells generated [17, 33]. According to the yields in the production of activated carbon from 1 kg of palm kernel 150 g of activated carbon are produced (Gómez *et al.*, 2010; Alvarez, 2019). This correspond to a production potential of activated carbon of 56482 ton.

Activated carbon is a material with very small pores whose walls are composed by laminar carbon (graphene), which gives them a high internal surface area and high adsorption capacity. Due to this it has been produced for several uses, such as, in medicine in the treatment of intoxications, in the processing of food for odor and taste removal, air cleaning, purification and/or treatment of waters. Additionally, it has been investigated for the storage of energy. Activated carbon consumption is led by Japan, followed by the United States and Western Europe where activated carbon is used primarily for treatment of water (Ahmed, 2016; Tan *et al.*, 2017; Marsh and Reinoso, 2006). To provide results that lead to practical solutions, it is necessary to determine the behavior of the activated carbon produced in the removal of paraquat diluted in water in conditions that resemble those presented in reality. One of the most frequent applications are fixed bed filters, which in most cases have the capacity to remove all the contaminants in continuous flow. The design process of these filters begins with the evaluation of the adsorption of a lab-scale fixed bed. The bed is subjected to a continuous flow of contaminated water and samples are taken at the exit in fixed time intervals. The concentration of the pollutant in the samples is plotted against time in a breakthrough curve (Worch, 2012; Çeçen and Aktas, 2011; Nakamura *et al.*, 1999; ASTM, 2008). The objective of this work is to evaluate the removal capacity of diluted paraquat in water in a bed of activated carbon from oil palm shells by the measurement of breakthrough curves. The process of evaluation of activated carbon in the removal of paraquat in the present work starts from the production of activated carbon from oil palm shells until the measurement of the breakthrough curves. Results are compared to those of the commercial activated carbon Hydrarffin® that is

currently used in the purification of water. The production of activated carbon starts from selecting the raw material, with characteristics such as hardness and materials with the capacity to develop an adequate porous structure. Typical raw materials include those that are abundant, with low ash content, low degradation, high hardness and high performance in the process of carbonized such as coal, vegetables, sludge and some wood. Sustainable raw materials for the production of activated carbons are coconut shells, bamboo, walnuts olive, oil palm shell and cultivated wood (Tan *et al.*, 2017).

2. Materials and methods

2.1. Raw materials and characterization

Activated carbon from oil palm shells (CA-CPA) is obtained in a two-step process. Oil palm shells were first dried until a water content of 10 % followed by carbonization. Carbonization process is performed in batches of 4230 g in a horizontal oven under nitrogen atmosphere. Parameters of the carbonization process were: average heating rate 4 °C/min, 0,9 L/min nitrogen flow, final temperature 500 °C and 30 min holding time at that temperature. Char yield was approximately 30 %. A final mass of 3000 g of char for further experimentation were produced. Activation is carried out using water vapor as activation agent. Three batches of 250 g each were performed. The char is heated until 850 °C under a nitrogen atmosphere (0,481 l/min). Thereafter the atmosphere is changed to water vapor were the sample is left until reaching the activation time. Once this process is finished the sample is left under nitrogen atmosphere until room temperature is reached. Activation time is set to 300 min according to preliminary tests that showed that with this time an activation grade of approximately 50 % can be reached. Final total mass of activated carbon ascends to 392 g equivalent to an activated carbon yield of 52,3 %. For comparison purposes experiments using a commercial activated carbon Hydrarffin® 8x30 from Donau Carbon GmbH (CAC) were performed. This activated carbon is used in water potabilization applications and has been used in experimental works with atrazine, herbicides of triazine and organic compounds, among others (Liddle, 1932; Zadaka *et al.*, 2009; Gardi *et al.*, 2015; Othman *et al.*, 2001; Aschermann *et al.*, 2018). This activated carbon is made from coconut shells through water vapor activation. Samples mean particle diameter were calculated from the granulometry analysis. In order to ensure the same flow conditions in the activated carbon bed the particle size distribution of sample CAC was adjusted according to that of sample CA-CPA. Both samples were characterized using the procedures presented in Table 1. Paraquat dichloride Hydrate - Pestanal® analytical standard, from Sigma Aldrich (CAS number 75365-73-0) was used as adsorbate.

2.2. Experimental facilities and procedures

Carbonization and activation were performed in a tubular reactor facility as shown in Figure 1. The numbers in the following description correspond to the ones in the figure. For the pyrolysis step a flow of nitrogen grade 5.0 is dosed

into the reactor during the whole experiment. For activation distilled water (1) is dosed into an evaporator (3) using a peristaltic pump (with maximal pumping capacity of 250 ml/h) (2). The water vapor is then directed into the tubular reactor (6 inch SCH60) that is placed inside an electric oven (4). Inside the reactor a system of baffles directs the flow in a way that it is forced to pass through the char sample as shown in Figure 1(b). Finally, the product gas and the remaining water leaves the reactor through a heated pipe (5) to a condenser and a torch.

The temperature inside the reactor is measured using a set of thermocouples T101 to T112 whose position is also shown in Figure 1(a). The sample is placed in the region where thermocouples T107, T108 and T109 are located as in this region a constant temperature profile over the sample is measured. The signals of the thermocouples are acquired using an acquisition module Agilent 34970A.

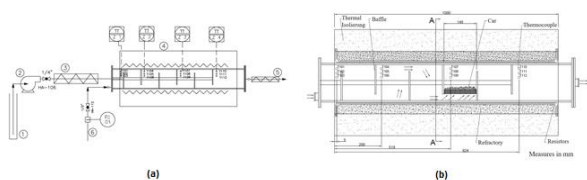


Figure 1. (a) Flow diagram of the experimental facility used for pyrolysis and activation. (b) Detail of the sample positioning in the horizontal tubular reactor during activation

Measurement of breakthrough curves is performed using the adsorption column facility presented in Figure 2(a). All metallic parts of the facility are made in stainless steel. For the circulation of the paraquat solution a peristaltic pump MasterFlex Model 77122-22 with tubing MasterFlex 95809-42 with internal diameter 2,06 mm. The storage tanks have a volume of 19,81 L with an internal diameter of 0,3 m and a height of 0,29 m. Figure 2(b) shows the overall dimensions of the column and the location of the activated carbon bed. The bed dimensions were established in a way that the radial ($d_R/d_p > 10$ [30,31]) and axial ($l_B/d_p > 200$ [20]) dispersions are minimized. Samples at different bed heights are collected using manual needle valves TM1, TM2 and TM3 are arranged on the column side.

Before the beginning of an experiment manual cleaning of all parts of the facility is performed with deionized water and the paraquat solution storage tank is filled with deionized water. The filling volume can be 5000 ml or 7000 ml depending on the experimental conditions. The system is put into operation using a water flow rate of 0,2415 ml/s during approximately 20 min in order to remove all residues that could remain in the ducts and particles of activated carbon in the bed from the previous experiment. The activated carbon bed is mounted according to the height defined in each experiment. The experimental facility allows to use one single 35 mm bed or 3 bed of 35 mm height each (as shown in Figure 2(b)). After the cleaning stage, the dead volume remains in the

feeding container and the test volume whose sum, for example, for experiment 1 is equal to 6131 ml. To this amount of deionized water is mixed the amount of paraquat in mg to get the final concentration used in each experiment. For example, for Experiment 1 with a concentration c_0 of paraquat of 5000 g/l, a quantity of 30,65 mg dissolved in 5 ml of deionized water in a beaker of 10 mL to the feeding container and mix for 3 min using a stirrer of glass. Finally, the feeding container is covered. After preparing the solution, the previously calibrated peristaltic pump is turned on using the same flow rate as for the cleaning stage and at the same time the stopwatch is started. The sample of the feeding concentration is taken, and then every 15 min the samples in each of the TM1, TM2 and TM3 valves for the experiments 1 and 3, for the other experiments only samples are taken in the TM1 valve. Each sample is taken in 10 ml Eppendorf tubes every 15 min and is labeled according to the time in which it was taken, the number of the experiment and the number of samplers. All samples are placed in a rack and stored for further analysis.

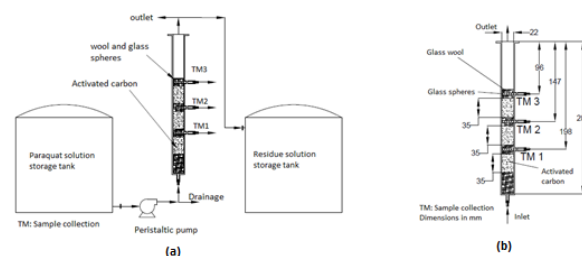


Figure 2. (a) Flow diagram of the adsorption column facility. (b) Dimensions of the adsorption column

2.3. Experimental plan

Experiments with variation in the bed height (35 mm or 3 x 35 mm), paraquat concentration (600 g/l, 2800 g/l and 5000 g/l) and time (340 s and 483 s) were performed for the two activated carbons used: commercial activated carbon (CAC) and activated carbon from oil palm shells (CA-CPA). Table 1 presents the experimental conditions used in each experiment.

The height of the carbon bed activated of 35 mm and the time of duration of the experiment of 480 min are used with the aim of obtaining a complete breakthrough curve. The volumetric flow rate of the column is determined according to the granulometry of the activated carbon and the peristaltic pump used in the existing assembly. As experiments were performed by maintaining the bed volume the mass of activated carbon in the bed is slightly different for both activated carbon samples as shown in Table 1.

2.4. Measurement of the paraquat concentration

The concentration of paraquat of each sample is determined using square wave voltammetry following the procedure of measurement of samples by standard addition, in which for each sample the entire assembly is performed by repeating the entire procedure. A

voltametric analyzer CV 50W BAS and Controlled Growth Mercury Electrode CGME, a boron-doped diamond electrode, D-629-SA windsorcient, a reference electrode Silver/Silver chloride 6 mm, a platin counter electrode, paraquat solution of 20400 µg/L, ammonium Buffer; 2,1208 g of ammonium sulfate and 200 µl NH₃. For the construction of calibration curves the working cell is

Table 1. Experimental plan

Parameter	Exp1	Exp2	Exp3	Exp4	Exp5	Exp6	Exp7
l_b [mm]	3x35	35	3x35	35	35	35	35
c_0 [µg/L]	5000	5000	5000	600	600	2800	2800
CA	CAC	CAC	CA-CPA	CAC	CA-CPA	CAC	CA-CPA
V_{ole} [mL]	5000	7000	7000	7000	7000	7000	7000
t_e [min]	340	483	483	483	483	483	483
t_l [min]	22,6	22,6	22,6	22,6	22,6	22,6	22,6
Δt_m [min]	15	15	15	15	15	15	15
d_p [mm]	1,35	1,35	1,35	1,35	1,35	1,35	1,35
Q_B [mL/s]	0,2415	0,2415	0,2415	0,2415	0,2415	0,2415	0,2415
T[°C]	20	20	20	20	20	20	20
m_{AC} /g	22,17	7,39	17,88	7,39	5,96	7,39	5,96

Table 2. Characterization of the activated carbon from oil palm shells and the reported values of the Hydrarfin® commercial activated carbon

Test	CAC	CA-CPA	Norm
$A_{BET}/m^2/g$	1074	1142	ISO 9277
Methylene blue/ml/g	195	187	NTC 4467
Water content/%	3,2	1.9	ASTM D2867-09
Volatile matter content/%	5,6	3.9	ASTM D5832-98
Ash content/%	1,6	6.9	ASTM D2866-11
pH	5,74	7.19	NTC 4467
Bulk density [kg/m ³]	556	448	NTC 4467
d_p /mm	1,35	1,35	Granulometry

2.5. Data analysis and calculations

Breakthrough curves are the representation of the variation of the concentration of a contaminant in a solution after passing a bed of activated carbon with time (Worch, 2012). The breakthrough point in the breakthrough curve is defined as the maximum acceptable concentration of paraquat at the column outlet according to paraquat concentration limits allowed in the United States and Colombia (200 g/l) [9, 10, 24]. From the analysis of the rupture curves, the parameters for the zone model of MTZ mass transfer that ends in defining the amount of paraquat removed up to the breaking point per unit mass of activated carbon (Worch, 2012). A comparison of the breakthrough curves of different adsorbents can be made by using the number of adsorbed fed beds (BV) of the specific performance (V_{sp}) instead of the duration of the experiment (t). The number of adsorbent beds is determined as the relationship between the volume of feed water at a given time (V_{al}) and the reactor volume (V_R). The specific performance (V_{sp}) represents the relationship between the volume of feed water at a given time (V_{al}) and the adsorbents mass (m_A) as shown in Eq. (1):

$$V_{sp} = \frac{V_{al}}{m_A} = \frac{Q_B t}{m_A} \quad (1)$$

assembled with 5 ml of pipetted supporting electrolyte. The base curve is measured by square wave voltammetry. Addition and measurement of 4 to 80 l aliquots of paraquat standard solution is performed with a concentration of 500 g/l, it is stirred at 300 rpm for 40 s.

The breakthrough curves are analyzed using the mass transfer zone model (MTZ). The characteristic parameters of the model are presented in Figure 3. Advance time (t_b) is defined as the time at which the concentration of the fed at the outlet of the bed was reached 50 % of the inlet concentration and the saturation time (t_s) is the time at which the outlet concentration of the feed has reached 95 % of the inlet concentration.

The difference between t_s and t_b is the mass transfer zone time (t_z). The stoichiometric time (t_{st}) is the theoretical time in which the bed will reach the equilibrium load (q_0) and can be calculated using Eq. (2). In this equation it is considered that the stoichiometric time is the time needed to reach the barycenter of the breakthrough curve,

$$t_{st} = \frac{q_0 m_A}{c_0 Q_B} \quad (2)$$

The velocity of the mass transfer zone can be determined according to Eq. (3):

$$v_z = \frac{h_z}{t_z} = \frac{h_b}{t_{st}} \quad (3)$$

The stoichiometric time can also be determined using a graphical analysis using the areas presented in Figure 3

and the determination of the symmetry factor F_s according to Eq. (4).

$$F_s = \frac{A_1}{A_1 + A_2} \quad (4)$$

Using the symmetry factor the stoichiometric time (t_{st}) and the mass transfer zone height (h_z) can be calculated according to Eq. (5) and Eq. (6),

$$t_{st} = t_b + F_s t_z \quad (5)$$

$$h_z = \frac{h t_z}{t_b + F_s t_z} \quad (6)$$

The advance time (t_b) and the saturation time (t_s) for a given bed height Eq. (7) and Eq. (8) are used,

$$t_b = \frac{h}{v_z} - F_s t_z \quad (5)$$

$$t_s = \frac{h}{v_z} + (1 - F_s) t_z \quad (6)$$

When scaling the data obtained in the laboratory, it must be considered that the parameters that must be maintained are the feeding concentration (c_0), the particle size of the adsorbent (d_p), and the interstitial velocity ($v_i = Q_B / (A_t \varepsilon_B)$) (Worch, 2012).

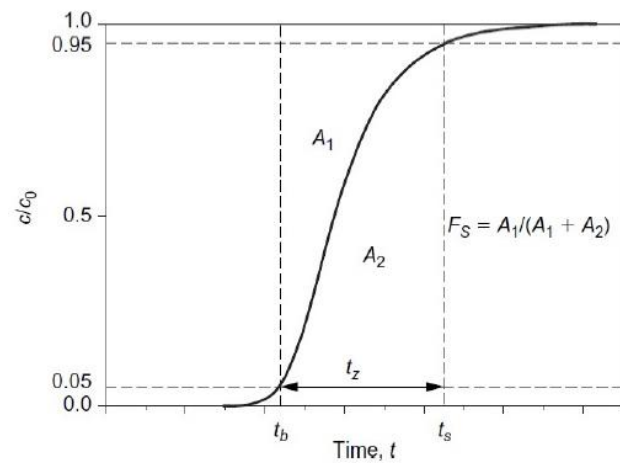


Figure 3. Characteristic parameters of a breakthrough curve and the symmetry factor (F_s) [35].

The removal capacity is the ratio between the amount of pollutant removed until reaching the breakthrough (A_{BP}) and the mass of the adsorbent (m_A) as shown in Eq. (7) (Namane and Hellal, 2006).

$$A_{BP} = \int_0^{V_{BP}} \frac{c_0 - c}{m_A} \quad (7)$$

With $V_{BP} = Q_B t_b$ is the volumen of solution that has passed through the bed up to the time where breakthrough point occurs.

3. Results and Discussion

3.1. Characterization of the activated carbons

Table 2 shows the results of the characterization of the produced activated carbon from oil palm shell and the the Hydriffin® commercial activated carbon. The N_2 -sorptionisothermen of both activated carbons shown in Figure 3 reveal a similar porous structure for the two samples.

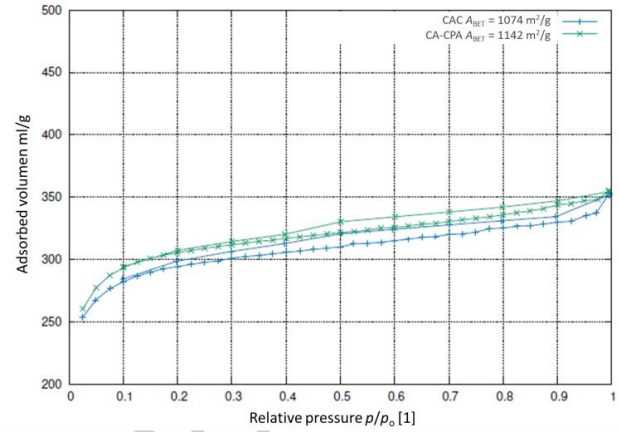


Figure 3. N_2 -Sorptionisothermen of the Hydriffin® commercial activated carbon (CA-CPA) and the activated carbon from oil palm shells (CAC).

3.2. Breakthrough curves

Figure 4 (a) and (b) show the breakthrough curves for Exp. 1 for the three bed heights corresponding to TM1, TM2 and TM3. In this experiment it was not possible to completely saturate the first bed, but at the first 30 min (corresponding to the first sample that was taken) a concentration of 203 g/l ($c/c_0 = 0,04$) is already observed. After 315 min the paraquat concentrations reaches a value of 2,652 g/l ($c/c_0 = 0,53$). In the second and third beds at 30 min a similar concentration of around 128 g/l is measured ($c/c_0 = 0,02$). The paraquat concentration increases continuously being more pronounced in the first bed as expected due to the higher paraquat concentration at its inlet. However, when the rupture curve is presented using the normalized through the specific performance (V_{sp}) it can be seen that the behavior in the three beds is very similar as shown in Figure 4(b). This behavior shows that for the same proportion of volume fed into the bed with respect to the mass of adsorbent, the same degree of saturation is obtained. Regarding the behavior of the activated carbon of oil palm shells CA-CPA shown in Figure 4(c) and (d) the paraquat concentrations in the fed are higher compared to the ones measured for CAC. The adsorption capacity of paraquat is then lower for CA-CPA than for CAC. Figure 4 (d) shows a similar behavior for the three heights studied.

The breakthrough curves for experiments 2 and 3 are presented in Figure 5. The duration time of Exp. 2 is estimated from experiment 1 obtaining 483 min for a complete breakthrough curve. For comparison the concentrations of the TM1 sampler from Exp. 3 are used.

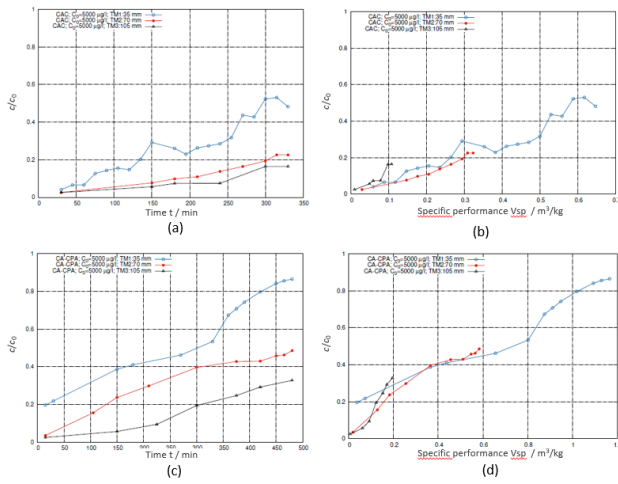


Figure 4. Breakthrough curves for CAC and CA-CPA according to: Exp. 1 (CAC) (a) and (b) and Exp. 3 (CA-CPA) (c) and (d).

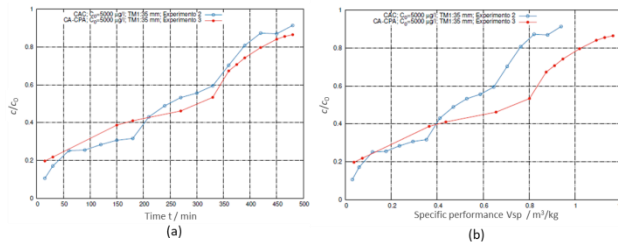


Figure 5. Breakthrough curves for CAC and CA-CPA according to: Exp. 2 (CAC) (a) and Exp. 3 (CPA) (b) (first bed).

The curves present a similar behavior. At the beginning of the experiment CAC shows better removal than CA-CPA. After 15 min the paraquat concentration of the solution in the CAC bed is 529 g/l ($c/c_0 = 0,1$) while that of the solution in the CA-CPA bed is 985 g/l ($c/c_0 = 0,15$). The final concentration of the solution in the CA-CPA bed is 4325 g/l ($c/c_0 = 0,86$) and that for the solution of the solution in the CAC bed is 4569 g/l ($c/c_0 = 0,91$). Both curves show an asymptotic behavior towards the inlet feeding concentration. Figure 5(b) shows the normalized curves of Exp. 2 and Exp. 3. Until a V_{sp} of $0,4 \text{ m}^3/\text{kg}$ both activated carbons show a similar behavior. After that CA-CPA shows a higher adsorption capacity of paraquat. In Figure 6 the influence of the paraquat inlet concentration on the breakthrough curves is observed. For both activated carbons the adsorption capacity of paraquat is lower at lower inlet concentrations. The influence is stronger for CA-CPA.

3.3. Parameters of the mass transfer model MTZ

Using the results of Exp. 2, Exp. 3, Exp. 4, Exp. 5, Exp. 6 and Exp. 7, the parameters of the MTZ model are determined. Initially F_s using the graphical method according to Eq. 4 is determined. The corresponding areas are calculated using a CAD program. Figure 7(a) shows that F_s decreases as the concentration decreases and it reaches a maximal value of approximately 0,5 for both activated carbons. The height of the mass transfer zone h_z , decreases with an increase in the concentration of

feeding, as shown in Figure 7(b). Figure 7(c) shows that the velocity of the mass transfer zone v_z decreases. Finally, in Figure 7(d) the amount of paraquat removed per unit mass until reaching the breakthrough point. For the highest concentration the removal capacity of CA-CPA is 11,8 % lower than the removal capacity of CAC.

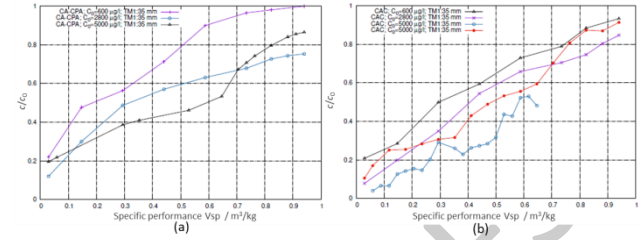


Figure 6. Breakthrough curves for CAC (b) and CA-CPA (a) for different inlet concentrations of paraquat in the solution.

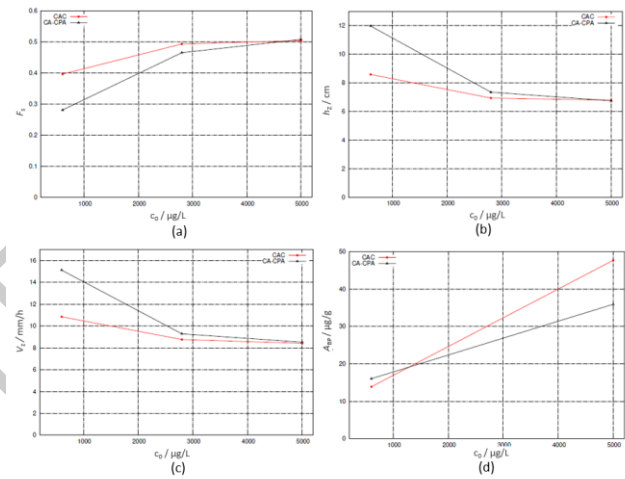


Figure 7. Parameters of the mass transfer zone model MTZ for the adsorption of paraquat in CAC and CA-CPA.

4. Conclusions

The activation of char from oil palm shell with a temperature of 850°C , steam flow of 20,68 l/min and activation time of 310 min allow to obtain activated carbon from oil palm kernels with a degree of activation of approx. 50 % and a specific BET surface area $1142 \text{ m}^2/\text{g}$. The produced activated carbon from oil palm shells produced to remove paraquat diluted in water through a fixed bed. Compared to the Hydriffin® activated carbon, removal capacities are similar and even higher for concentrations usually found in natural water samples. The removal capacity of the activated carbon of oil palm kernels for paraquat diluted in water at concentrations between 600 g/l and 5000 g/l are between 16,08 g/g and 35,95 g/g respectively. Using activated carbon of oil palm shells with a specific performance of $V_{sp} = 0,00607 \text{ m}^3/\text{kg}$ or smaller and with feeding concentrations from 600 g/l to 5000 g/l, lower than 200 g/l are obtained. This allows to conclude that this activated carbon can be applied in systems for the construction of filters for removal of paraquat diluted in water.

Nomenclature

Symbol

A	Ash content, wt.-%
d	Diameter, mm
h	Bed height, cm
l	Length, mm
M	Moisture, wt.-%
m	Mass, g
Q	Volumetric flow rate, m ³ /s
T	Temperature, °C
t	Time, s
V	Volume, m ³
v	Velocity/m/s
κ	Heating rate, K/min

Subscript

B	Bed
f	Free
t	Cross-section
R	Reactor

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