

# Adsorption of 2,4-dichlorophenoxyacetic acid (2,4D) on sargassum activated carbon

Omar Paino Perdomo<sup>a</sup>, Luis Enrique Rodríguez de Francisco<sup>a</sup>, José Aceituno<sup>a</sup>, Yeray Álvarez Galván<sup>b,c</sup>, Nicolas Brehm<sup>b</sup>, Christelle Yacou<sup>c</sup>, Sarra Gaspard<sup>c</sup>, Michel Manduca-Artiles<sup>d</sup>, Andy Machín Garriga<sup>d</sup>, Ulises Jáuregui-Haza<sup>a,\*</sup>

<sup>a</sup> Instituto Tecnológico de Santo Domingo (INTEC), Avenida de Los Próceres #49, Los Jardines del Norte 10602, Santo Domingo, Dominican Republic

<sup>b</sup> NBC SARL, 8 rue Saint Cyr, 5 Résidence Océane 97300 Cayenne. French Guyana

<sup>c</sup> Laboratoire COVACHIMM-M2E, EA 3592 Université des Antilles, BP 250, 97157 Pointe à Pitre, Cedex. Guadeloupe, French West-Indies

<sup>d</sup> Instituto Superior de Tecnologías y Ciencias Aplicadas, Universidad de La Habana, Quinta de los Molinos, Plaza de la Revolución, La Habana, Cuba.

*Adsorción de ácido 2,4-diclorofenoxiacético (2,4D) en carbón activado de sargazo*

*Adsorció d'àcid 2,4-diclorofenoxiacètic (2,4D) sobre carbó activat de sargàs*

RECEIVED: 17 JULY 2022; ACCEPTED: 12 APRIL 2023; DOI: <https://doi.org/10.55815/417977>

## ABSTRACT

The production of activated carbon was carried out by impregnating the sargassum with a 85%  $H_3PO_4$  solution in a mass ratio of 1/3 sargassum/  $H_3PO_4$ , with an impregnation time of 15 hours. The production of activated carbon from sargassum was carried out in a pyrolytic muffle furnace with a controlled nitrogen atmosphere. Sargassum samples were collected on the beaches of the Dominican Republic. Sargassum activated carbon has a specific surface area of 754  $m^2/g$  and the 2,4-D adsorption was pH dependent.

**Keywords:** adsorption, 2,4-dichlorophenoxyacetic acid, activated carbon, sargassum.

## RESUMEN

La producción de carbón activado se realizó mediante la impregnación del sargazo con una solución de  $H_3PO_4$  al 85% en una relación másica de 1/3 sargazo/ $H_3PO_4$ , con un tiempo de impregnación de 15 horas. La producción de carbón activado a partir de sargazo se realizó en un horno de mufla pirolítica con atmósfera de nitrógeno

controlada. Se recolectaron muestras de sargazo en las playas de República Dominicana. El carbón activado de sargazo tiene un área de superficie específica de 754  $m^2/g$  la adsorción de 2,4-D dependía del pH.

**Palabras clave:** adsorción, ácido 2,4-diclorofenoxiacético, carbón activado, sargazo.

## RESUM:

La producció de carbó actiu es va dur a terme impregnant el sargàs amb una solució d' $H_3PO_4$  al 85% en una proporció de massa d'1/3 sargas/ $H_3PO_4$ , amb un temps d'impregnació de 15 hores. La producció de carbó actiu a partir de sargas es va dur a terme en un forn de mufla pirolític amb una atmosfera de nitrogen controlada. Es van recollir mostres de sargassos a les platges de la República Dominicana. El carbó activat de sargassó té una superfície específica de 754  $m^2/g$  i l'adsorció de 2,4-D depenia del pH.

**Paraules clau:** adsorció, àcid 2,4-diclorofenoxiacètic, carbó actiu, sargàs



\*Corresponding author: [ulises.jauregui@intec.edu.do](mailto:ulises.jauregui@intec.edu.do)

## INTRODUCTION

The intensive development of agriculture has led to an overconsumption of chemicals, with the consequent contamination of soils and water. Among these chemicals are phenoxyalkanoic herbicides, with 2,4-dichlorophenoxyacetic acid (2,4-D) being the most widely used among them<sup>1,2</sup>. The 2,4-D has been classified as a refractory pollutant by the Environmental Protection Agency (EPA)<sup>3</sup>, due to its high solubility in water and slow degradation by biological processes<sup>4</sup>. 2,4-D can negatively affect aquatic life in water bodies and can cause chromosomal aberrations in human lymphocytes<sup>5</sup>.

For this reason, the World Health Organization (WHO) classified it as moderately toxic (Class II) and, therefore, established its maximum allowed concentration in drinking water at 100 ppb<sup>6</sup>. The content of 2,4-D in surface and groundwater has been reported to be greater than 0.1 µg/L<sup>7</sup>.

It is for all of the above, that studies for the decontamination of waters contaminated with 2,4-D have been prioritized at the international level. Among the most studied processes are the advanced oxidation processes<sup>8-17</sup> and adsorption<sup>18-32</sup>.

However, it should be noted that, although advanced oxidation processes guarantee the total degradation of the herbicide, these are still very expensive processes to treat large volumes of contaminated water. Therefore, an alternative is the combination of processes, where adsorption is initially used, to concentrate the contaminant, and then advanced oxidation processes.

Adsorption is considered as a flexible, adaptable, selective and highly efficient method to eliminate micro-contaminants<sup>33</sup>. Among the adsorbents used for decontamination of waters with 2,4-D are activated carbons (CA) obtained from agricultural residues<sup>18, 21, 22, 25-27, 29, 31, 34, 35</sup>, derived from cellulose<sup>32</sup>, composites of different nature<sup>23,24,30,36</sup>, polymers<sup>37</sup>, and graphene nanospheres<sup>20</sup>.

We propose here, the use of *Sargassum spp.*, as activated carbon precursor. Indeed, the beaches of the insular and continental Caribbean have experienced increasing floods of large masses of pelagic algae of the species *S. natans* and *S. fluitans* in the last decade<sup>40-46</sup>. These massive floods to the coasts have had many environmental, health and financial implications<sup>42,43,45-53</sup>. Therefore, it is important to try to valorize sargassum and among the possible alternatives is obtaining activated.

Several research teams have reported the use of activated carbon obtained from sargassum for the adsorption of heavy metals<sup>55-59</sup>, carbon dioxide<sup>59-60</sup>, colorants<sup>61</sup>, pollutants from the oil industry<sup>62</sup> and caffeine<sup>63</sup>, but there is no known previous study that has evaluated the adsorption of 2,4-D in sargassum activated carbon. Therefore, the objective of this study the adsorption 2,4-D herbicide activated carbon prepared from sargassum collected from the coasts of the Dominican Republic.

## MATERIALS AND METHODS CHEMICAL PRODUCTS

The 2,4-D (purity ≥ 99.0%) and the other chemical reagents were supplied by Sigma-Aldrich, all of analytical quality. The necessary solutions for the adsorption experiments were obtained by dilution with deionized water.

### Collection and pre-treatment of sargassum

The species *Sargassum fluitans* was collected from the beaches of Punta Cana (Higüey province, Dominican Republic) in the years 2017, 2018 and 2019. The sargassum was rinsed with seawater to remove the sand during collection. Subsequently, the sargassum was washed with tap water, fresh water, with the aim of carefully removing inorganic residues, mainly sand and salt, and separating the sargassum algae from any other type of algae. The washed sargassum was dried in the open air in order to remove the most possible amount of water before total drying in an NBC SARM muffle furnace for 48h at 85°C.

The dried sargassum was ground with a mortar and an automatic cutter and sieved in a range of 0.5 to 1.5 mm. Grinding sargassum not only reduces particle size, it also separates fine grains of sand and salt that pass through the 0.5 mm filter.

### Obtaining activated carbon from sargassum

The production of activated carbon was carried out by impregnating the sargassum with an 85% H<sub>3</sub>PO<sub>4</sub> solution in a mass ratio of 1/3 sargassum/H<sub>3</sub>PO<sub>4</sub>. The impregnation time was 15 hours. After the impregnation time, the sargassum and acid mixture was introduced into the muffle furnace in porcelain crucibles. The production of activated carbon from sargassum was carried out in a pyrolytic muffle furnace with a controlled atmosphere of nitrogen, designed and built by the company NBC SARM. The furnace is arranged in the facilities of the Instituto Tecnológico de Santo Domingo (INTEC) with the objective of carrying out experimental production of activated carbons. The pyrolysis was programmed by means of a PLC (Programmable Logic Controller), temperature increase rate of 4.3 °C/min., to reach a maximum heating temperature of 600 °C. The sample was then pyrolyzed at this temperature during 1 h.

The cooling of the oven is carried out progressively, so that its total cooling is achieved after 15 hours after the disconnection of its internal resistances. The activated carbon produced is then ground and washed with distilled water until neutral pH is reached. Better washes are achieved when the water is heated to 60 °C and the sample is allowed to stir for 30 min. Multiple washes had to be performed, as many as necessary. After washing, the activated carbon drying was carried out in an oven at 110 °C for 72 hours.

## Characterization of activated carbon

The specific surface area and pore volume of the AC were determined from the nitrogen adsorption isotherms at 77 K, using the analyzer of the series SORPTOMATIC 1990. The BET specific surface area was calculated from the nitrogen isotherm for relative pressures between 0.10 and 0.22<sup>64</sup>.

To quantify the pH at the zero charge point ( $pH_{PZC}$ ) 0.1 g of carbon was added to 20 mL of 0.1 M NaCl solution at different initial pH values between 2 and 11, which is achieved with the addition of aqueous solutions of NaOH or 0.5M HCl. The vessels were placed on a thermostated orbital shaker at 25 °C for 24 hours at 150 rpm, after which the pH was measured<sup>65</sup>.

The acid-base properties of AC were determined according to the procedure proposed by Boehm<sup>66</sup>. 50 mL of 0.05 M NaOH solution was prepared to determine the acid groups and 50 ml of 0.05 M HCl solution to determine the basic groups. Those solutions were contacted with 0.5 g of AC. The bottles were closed and shaken for 2 days. The charcoal was then separated from the solution with a 0.45 µm filter and 10 mL of each filtrate was titrated with HCl or NaOH (0.05 M), as appropriate.

## AC pretreatment for adsorption studies

The AC particle size was reduced to 125 µm. To remove moisture from the AC, it was left for 48 h at 70 °C in a vacuum desiccator, and then was deposited in sealed jars.

## Kinetic study

*Determination of the mass of AC and the time of maximum adsorption of 2,4-D in AC*

To determine the adsorption curve, different masses of AC (3, 5, 9, 15, 20 mg) are placed in 100 mL glass bottles with 50 mL of the 2,4-D solution at 13 mg / L, with an initial pH of 2.5 adjusted with a 10% solution of H<sub>2</sub>SO<sub>4</sub>. The samples are mechanically shaken and kept at a temperature of 25 ± 0.1 °C, for a period of 2 hours. Every 10 min an aliquot of 1 mL was taken for analysis by UV spectrophotometry. The mass of AC that was selected depended on the absorption of 2,4-D and the detection limit of the method used to determine the concentrations of the analytes in solution. For the 3 mg mass, the study was performed in triplicate with an average relative error of determination of the concentration in the aqueous phase of 4.7%.

*Influence of pH on the adsorption of 2,4-D in AC*

The pH of the solution is usually an important factor, as it influences the surface charge of the adsorbent and speciation of the adsorbate in the solution.

Taking into account the results obtained for the kinetic studies, a AC mass of 3 mg was selected. The weighed mass was transferred to 100 mL bottles with 50 mL of 2,4-D solution of 20 mg/L concentration at different pHs (2.5, 5, 7 and 9). The samples are

mechanically shaken and kept at a temperature of 25 ± 0.1 °C, for a period of 4 hours. At the end of this time, the solutions were centrifuged and an aliquot of 1 mL was taken to determine 2,4-D concentration by spectrophotometry. The study at pH 2.5 was performed in triplicate with an average relative error of 5% of the concentration in the aqueous phase.

## 2,4-D adsorption isotherm in AC

The procedure described for the pH study is used, for different initial concentrations of 2,4D between 0.5 and 20 mg/L. The study was carried out in triplicate with an average relative error of determination of the concentration in the aqueous phase of 5.8%.

*Modeling of adsorption isotherms*

Table 1 shows the models used in the modeling of the adsorption isotherm.

The adjustment of the isotherm models to the experimental data was performed using a nonlinear regression algorithm. The procedure for calculating the value of the isotherm parameters is to minimize the sum of residual squares (Eq. 9).

$$RSS = \sum_{i=1}^n (q_{exp,i} - q_{t,i})^2 \quad (9)$$

Where  $q_{exp,i}$  y  $q_{t,i}$  are the calculated and experimental values for each point respectively.

Akaike's methodology tries to find the model that best explains the data with a minimum of free parameters<sup>74</sup>. Assuming that the error in the models is normally and independently distributed, the AIC is defined by equation 10.

$$AIC = n \ln \left( \frac{RSS}{n} \right) + 2k \quad (10)$$

Where k is the number of parameters in the model and n is the number of data. The preferred model is the one with the lowest AIC value. When n is small compared to k, the AIC second order correction (AICc) is more accurate (Eq. 11).

$$AICc = AIC + \frac{2k(k+1)}{n-k-1} \quad (11)$$

The average relative error is calculated by equation 12.

$$AARE = \frac{100}{n} \sum_{i=1}^n \frac{|q_{exp,i} - q_{t,i}|}{q_{exp,i}} \quad (12)$$

## Determination of the concentration of 2,4-D

The 2,4-D standard solution was measured in a UV-SECOMAM spectrophotometer at a wavelength of 230 nm. 2,4-D solutions were prepared in a concentration range of (0.5-20 mg/L).

**Table 1.** Models of adsorption isotherms:  $q$  is the amount adsorbed of the compound in equilibrium per unit of adsorbent,  $q_{max}$  is the capacity of AC,  $C$  is the concentration of adsorbate in equilibrium in aqueous phase  $\chi$  is the adsorbate interaction parameter -adsorbate,  $v$  is the heterogeneity parameter,  $K$  are already model parameters.  $R$  is the parameter that considers the adsorbate-adsorbate interaction at a site in the Ruthven model,  $R_2$  and  $R_3$  are the parameters corresponding to the binary and ternary adsorbate-adsorbate interactions in a box, respectively for the Ruthven model.

Model	
Langmuir <sup>67</sup>	$q = q_{max}KC/(1 + KC)$ (1)
Jovanovic <sup>68</sup>	$q = q_{max}(1 - e^{-(KC)})$ (2)
Fowler <sup>69</sup>	$q = q_{max}KC/(e^{-\chi \frac{q}{q_{max}}} + KC)$ (3)
Freundlich <sup>70</sup>	$q = KC^v$ (4)
Jovanovic- Freundlich <sup>71</sup> (JF)	$q = q_{max}(1 - e^{-(aC)^v})$ (5)
Fowler-Guggenheim/Langmuir-Freundlich <sup>72</sup> (FG/LF)	$q = \frac{q_{max} \left( aC e^{\chi \frac{q}{q_{max}}} \right)^v}{1 + \left( aC e^{\chi \frac{q}{q_{max}}} \right)^v}$ (6)
Ruthven $n=2$ <sup>73</sup>	$q = \frac{q_{max}(KC + R(KC)^2)}{1 + KC + \frac{R}{2}(KC)^2}$ (7)
Ruthven $n=3$ <sup>73</sup>	$q = \frac{q_{max}(KC + R_2(KC)^2 + \frac{R_3}{2}(KC)^3)}{1 + KC + \frac{R_2}{2}(KC)^2 + \frac{R_3}{6}(KC)^3}$ (8)

## RESULTS

### Characteristics of activated carbon.

Sargassum activated carbon has a specific surface of 754 m<sup>2</sup>/g, within the range of the specific surface values of other activated carbons obtained from different varieties of sargassum, which range between 5.8 and 1300 m<sup>2</sup>/g<sup>57-62</sup>. The total pore volume is 0.95 cm<sup>3</sup>/g with a prevalence of mesopores (0.63 cm<sup>3</sup>/g) over micropores (0.27 cm<sup>3</sup>/g). The Boehm test gave 5.01 mmol /g of acid groups with only 0.07 mmol/g of basic groups. This value, together with a pHPZC of 2.71, certify the acidic nature of the AC obtained. A more detailed description of the physical-chemical properties of this AC were published by Francoeur *et al.*<sup>63</sup>

### Kinetic study for the determination of the mass of AC and the time of the maximum adsorption of 2,4-D in AC

Figure 1 shows the adsorption curve over time for 2,4-D for five different masses of activated carbon. The highest adsorption capacity was achieved when 3 mg of activated carbon were used, so subsequent studies were carried out with that amount of AC. As for the adsorption time, it takes more than two hours to reach equilibrium, so subsequent studies were carried out at 4 hours. The equilibration time for the adsorption of the herbicide on different adsorbents varies from 30 minutes to 20 hours<sup>18,22,25,27,30,32</sup>.

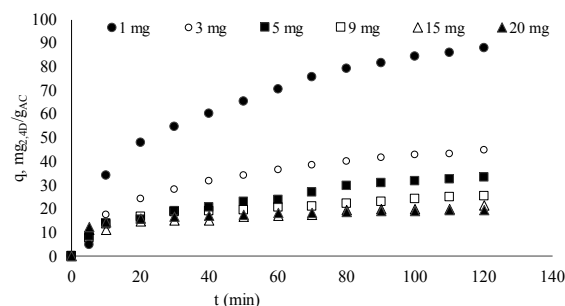
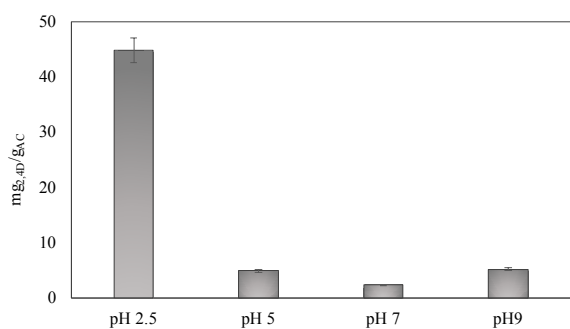


Figure 1. Kinetic study of 2,4-D adsorption in AC. With an initial concentration of 13 mg/L and a variable AC mass between (3-20 mg), at a pH = 2.5, with a stirring speed of 180 rpm and a temperature of 25 °C.

The effect of the contact time shows that the adsorption of 2,4-D in the initial stage is faster, which can be explained because initially there are a large number of vacant sites available and the concentration gradient is also high, which results in faster absorption. However, in the subsequent adsorption stage, the removal rate gradually decreases with time until equilibrium is reached. With increasing adsorption time, the amount of vacant sites on the AC surface gradually decrease. The remaining vacant sites are difficult to fill due to the repulsive forces between the 2,4-D molecules on the solid surface and those in the liquid phase, which ultimately slow down the rate of adsorption. This behavior varies depending on the nature of the surface of each AC<sup>35</sup>.

### Influence of the pH of the adsorption of 2,4-D on AC

The charges developed on the surface of the adsorbent and the degree of ionization of the adsorbate are functions of pH, therefore, the effect of the pH of the solution on the adsorption of 2,4-D was studied for pH between 2 and 9. Figure 4 shows amount of 2,4-D adsorbed per gram of AC at different pH. The results indicated a reduction in the adsorption capacity of 2,4-D with an increase in the pH of the solution. This is due to the combined effect of the zero charge point ( $\text{pH}_{\text{PZC}} = 2.71$ ) and the pH of the solution on the loads developed on the adsorbent surface. When the pH in the medium is less than  $\text{pH}_{\text{PZC}}$ , the surface of the AC is positively charged and at pH greater than  $\text{pH}_{\text{PZC}}$  the surface of the AC is negatively charged. On the other hand, the pKa of 2,4-D is 2.8<sup>18</sup>, therefore, according to the relationship between pH and pKa, the molecular form of 2,4-D is expected to be greater than that of the anionic form at acidic pH. Thus, the adsorption of 2,4-D in molecular form on the surface of the AC is expected to be due to weak van der Waals interactions. Therefore, the elimination of 2,4-D is greater at a lower pH, in this case 2.5. (Figure 2).



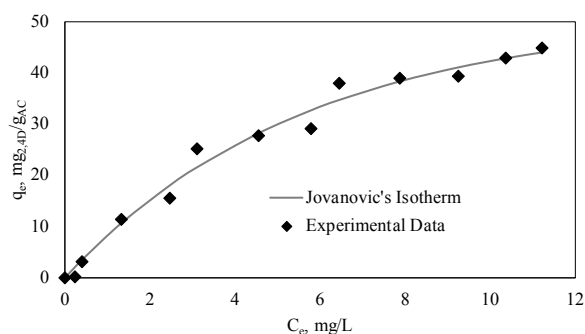
**Figure 2.** Influence of pH on adsorption at 25 °C and 4 hours.

A similar behavior was observed by Deokar *et al.*<sup>18</sup> when studying the adsorption of 2,4-D on bagasse ash, and demonstrating that the adsorption of the pesticide reached its maximum value at a pH of 2. On the other hand, when studying the Herbicide adsorption on rice straw AC best adsorption was achieved at pH 3, in a study interval between 3 and 10<sup>27</sup>. Even when using a completely different adsorbent, modified magnesium ferite nanoparticles with amino surface groups, the highest adsorption of 2,4-D is achieved at an acidic pH of 3, after having explored the pH zone of 3 to 12<sup>30</sup>.

### 2,4-D adsorption isotherm in AC.

For the determination of the isotherm, the optimum pH selected in the previous study was started. Figure 3 shows the adsorption isotherm of 2,4-D on AC. The maximum estimated adsorption capacity is 51 mg<sub>2,4D</sub>/g<sub>AC</sub>. C considering that the maximum adsorption capacities of 2,4-D on activated carbons obtained from different biomass sources ranges from 0.9 to 574.7 mg/g<sub>AC</sub><sup>18,21,22,25-27,29,34</sup>, the values obtained for this sargassum activated carbon is low. The highest adsorption values, between 134.8 and 574.7 mg/g<sub>AC</sub>, were obtained for activated carbons from willow, linseed, hemp<sup>25</sup>, rice

husk<sup>27</sup>, granulated activated carbon of biomass<sup>34</sup> and orange peel<sup>26</sup>.



**Figure 3.** The 2,4-D adsorption isotherm in AC at 25 °C and 4 hours.  $q_e$  is the amount of compound adsorbed in equilibrium per unit amount of adsorbent (mg/L);  $c_e$  is the equilibrium aqueous phase adsorbate concentration (mg/L).

Several studies have been conducted to elucidate the adsorption mechanism of many molecules, including pesticides and herbicides, on different adsorbents. These publications reveal that the adsorption of organic molecules from dilute aqueous solutions in carbon materials is a complex interaction between electrostatic and non-electrostatic interactions and that both interactions depend on the characteristics of the adsorbent and adsorbate, as well as the chemical properties of the solution<sup>75-78</sup>. A variety of physicochemical forces, such as van der Waals, H-binding, dipole-dipole interactions, ion exchange, covalent bonding, cation bridging, and water bridging, can be responsible for the adsorption of organic compounds on activated carbon<sup>75,77</sup>. Taking into account the results obtained, and those reported by other authors, the adsorption of 2,4-D in the sargassum AC seems to have a physical nature with the prevalence of weak electrostatic interactions of the Van der Waals type<sup>18,21,22</sup>.

## CONCLUSIONS

The adsorption of the herbicide 2,4-dichlorophenoxyacetic acid from aqueous solutions in activated carbon obtained from sargassum was studied. The activated carbon obtained by activation with phosphoric acid has a specific surface of 754 m<sup>2</sup>/g, a total porous volume is 0.95 cm<sup>3</sup>/g and a  $\text{pH}_{\text{PZC}}$  of 2.71. 2,4-D adsorption was pH dependent, with a decrease in adsorption capacity as the initial pH of the solution increased from 2 to 9. The adsorption isotherm showed a maximum adsorption capacity of 51 mg of 2,4-D/g AC. This value is lower than that obtained for other activated carbons obtained from agricultural or forest residues. Jovanovic's isotherm model provided a better correlation of experimental adsorption equilibrium data.

## ACKNOWLEDGMENTS

On behalf of the research team, we thank the technical and human support of the COVACHIM-M2E laboratory (Université des Antilles, Guadeloupe, France) for their contribution, facilitating the analysis teams and personnel necessary to carry out the studies required for the development of this research. Likewise, we thank the research team of InSTEC (Higher Institute of Technologies and Applied Sciences, University of Havana, Cuba), for their collaboration in conducting part of experimental work. Also, we thank Instituto Tecnológico de Santo Domingo (INTEC) for their contribution in the collection and treatment of sargassum, and for their active participation in the management of this research project. We are very grateful to Yolanda León and Virgilio Miniño for providing sargassum samples. This work received the financial support of ONAPI and FONDOCYT through the project: “*Producción de carbón activado a partir de sargazo y estudio de su potencial para el tratamiento de efluentes*”. Lastly, we thank the ANRT (National Association for Research and Technology in France) for their role as funder of Yeray Álvarez Galván’s doctoral thesis under the CIFRE agreement (ANRT - NBC SARL).

## BIBLIOGRAPHIC REFERENCES

1. Botrè, C., Botrè, F., Mazzei, F. & Podestà, E. (2000). Inhibition-based biosensors for the detection of environmental contaminants: determination of 2, 4-dichlorophenoxyacetic acid, *Environ. Toxicol. Chem.*, 19: 2876–2881.
2. Loos, R., Locoro, G., Comero, S., Contini, S., Schweisig, D., Werres, F., Balsaa, P., Gans, O., Weiss, S., Blaha, L., Bolchi, M. & Gawlik, B. M. (2010). Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water, *Water Res.*, 44: 4115–4126.
3. Registration Eligibility Decision (RED) (2005). 2,4-D, EPA 738-R-05-002, U.S. Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances, Office of Pesticide Programs, U.S. Government Printing Office.
4. Laganà, A., Bacaloni, A., De Leva, I., Faberi, A., Fago, G. & Marino, A. (2002). Occurrence and determination of herbicides and their major transformation products in environmental waters, *Anal. Chim. Acta*, 462: 187–198.
5. Xi, Y., Mallavarapu, M. & Naidu, R. (2010). Adsorption of the herbicide 2,4-D on organo-palygorskite, *Appl. Clay Sci.* 49: 255–261.
6. WHO (2002). The World Health Report: Reducing Risks, Promoting Healthy Life, World Health Organization.
7. Muszyński, P., Brodowska, M. S. & Paszko, T. (2020). Occurrence and transformation of phenoxy acids in aquatic environment and photochemical methods of their removal: a review. *Env. Sci. Pol. Res.*, 27:1276–1293.
8. Piera, E., Calpe, J. C., Brillas, E., Domènech, X. & Peral, J. (2000). 2,4-Dichlorophenoxyacetic acid degradation by catalyzed ozonation: TiO<sub>2</sub>/UVA/O<sub>3</sub> and Fe(II)/UVA/O<sub>3</sub> systems, *Appl. Catal. B-Environ*, 27: 169–177.
9. Yu, Y., Jun, M. & Hou, Y. (2006). Degradation of 2,4-dichlorophenoxyacetic acid in water by ozone-hydrogen peroxide process, *J. Environ. Sci.*, 18: 1043–1049.
10. Guzmán, C., Del Ángel, G., Gómez, R., Galindo-Hernández, F. & Ángeles-Chavez, C. (2011). Degradation of the herbicide 2,4-dichlorophenoxyacetic acid over Au/TiO<sub>2</sub>/CeO<sub>2</sub> photocatalysts: effect of the CeO<sub>2</sub> content on the photoactivity, *Catal. Today*, 166: 146–151.
11. García, O., Isarain-Chavez, E., García-Segura, S., Brillas, E. & Peralta-Hernández, J. M. (2013). Degradation of 2,4-dichlorophenoxyacetic acid by electro-oxidation and electro-Fenton/BDD processes using a pre-pilot plant. *Electrocatal.*, 4: 224–234.
12. Gilliard, M. B., Martín, C. A., Cassano, A. E., Lovato, M. E. (2013). Reaction kinetic model for 2,4-dichlorophenoxyacetic acid decomposition in aqueous media including direct photolysis, direct ozonation, ultraviolet C, and pH enhancement, *Ind. Eng. Chem. Res.*, 52: 14034–14048.
13. Maya-Treviño, M. L., Guzmán-Mar, J. L., Hinojosa-Reyes, L., Ramos-Delgado, N. A., Maldonado, M. I. & Hernández-Ramírez, A. (2014). Activity of the ZnO–Fe<sub>2</sub>O<sub>3</sub> catalyst on the degradation of Dicamba and 2,4-D herbicides using simulated solar light, *Ceram. Int.*, 40: 8701–8708.
14. Cruz-González, G., Julcour, C., Chaumat, H., Jáuregui-Hazab, Ul., & Delmasa. H. (2018). Degradation of 2,4-dichlorophenoxyacetic acid by photolysis and photo-Fenton oxidation. *J. Env. Chem. Eng.*, 6: 874–882.
15. Zhao, G., Chen, X., Zou, J., Li, C., Liu, L., Zhang, T., Yu, J. & Jiao, F. (2018). Activation of peroxy-monosulfate by Fe<sub>3</sub>O<sub>4</sub>–Cs x WO<sub>3</sub>/NiAl layered double hydroxide composites for the degradation of 2, 4-dichlorophenoxyacetic acid. *Ind. Eng. Chem. Res.*, 57 (48): 16308–16317.
16. Mehralipour, J. & Kermani, M. (2019). Optimization of the Ultrasonic-Electroproxone Process Via Graphene-Titanium Electrodes in Removal of 2, 4 D from Synthetic Wastewater by RSM. *J. Env. Health Eng.*, 7(1): 11-28.
17. Rajah, Z., Guiza, M., Solís, R. R., Rivas, F. J. & Ouederni, A. (2019). Catalytic and photocatalytic ozonation with activated carbon as technologies in the removal of aqueous micropollutants. *J. Photochem. Photobiol. A: Chemistry*, 382: 111961.
18. Deokar, S. K., Mandavgane, S. A. & Kulkarni, B. D. (2016). Adsorptive removal of 2, 4-dichlorophenoxyacetic acid from aqueous solution using bagasse fly ash as adsorbent in batch and packed-bed techniques. *Clean Tech. Env. Policy*, 18(6): 1971–1983.
19. Kuśmierk, K., Szala, M. & Świątkowski, A. (2016). Adsorption of 2, 4-dichlorophenol and 2, 4-dichlorophenoxyacetic acid from aqueous solutions on

- carbonaceous materials obtained by combustion synthesis. *J. Taiwan Inst. Chem. Eng.*, 63: 371-378.
20. Kamaraj, R., Pandiarajan, A., Gandhi, M. R., Shibayama, A. & Vasudevan, S. (2017). Eco-friendly and easily prepared graphenenanosheets for safe drinking water: removal of chlorophenoxyacetic acid herbicides. *Chem. Select*, 2 (1): 342-355.
  21. Kirbıyık, C., Pütün, A. E. & Pütün, E. (2017). Equilibrium, kinetic, and thermodynamic studies of the adsorption of Fe (III) metal ions and 2, 4-dichlorophenoxyacetic acid onto biomass-based activated carbon by ZnCl<sub>2</sub> activation. *Surf. Interf.*, 8: 182-192.
  22. Mandal, S., Sarkar, B., Igalavithana, A. D., Ok, Y. S., Yang, X., Lombi, E. & Bolan, N. (2017). Mechanistic insights of 2, 4-D sorption onto biochar: Influence of feedstock materials and biochar properties. *Biores. Techn.*, 246: 160-167.
  23. Sarker, M., Ahmed, I. & Jung, S. H. (2017). Adsorptive removal of herbicides from water over nitrogen-doped carbon obtained from ionic liquid@ ZIF-8. *Chem. Engin. J.*, 323: 203-211.
  24. Zhao, R., Li, X., Sun, B., Ji, H. & Wang, C. (2017). Diethylenetriamine-assisted synthesis of amino-rich hydrothermal carbon-coated electrospun polyacrylonitrile fiber adsorbents for the removal of Cr (VI) and 2, 4-dichlorophenoxyacetic acid. *J. Colloid Interf. Sci.*, 487: 297-309.
  25. Doczekalska, B., Kuśmierk, K., Świątkowski, A. & Bartkowiak, M. (2018). Adsorption of 2, 4-dichlorophenoxyacetic acid and 4-chloro-2-metylphe-noxyacetic acid onto activated carbons deriv Lin ed from various lignocellulosic materials. *J. Env. Sci. Health, Part B*, 53(5): 290-297.
  26. Pandiarajan, A., Kamaraj, R., Vasudevan, S., & Vasudevan, S. (2018). OPAC (orange peel activated carbon) derived from waste orange peel for the adsorption of chlorophenoxyacetic acid herbicides from water: adsorption isotherm, kinetic modelling and thermodynamic studies. *Biores. Techn.*, 261, 329-341.
  27. Abdel Daïem, M.M., Sánchez-Polo, M., Rashed, A. S., Kamal, N., & Said, N. (2019). Adsorption mechanism and modelling of hydrocarbon contaminants onto rice straw activated carbons. *Polish J. Chem. Techn.*, 21(4): 1-12.
  28. Coelho, E. R. C., Brito, G. M. D., Frasson Lou-reiro, L., Schettino Jr, M. A. & Freitas, J. C. C. D. (2020). 2, 4-dichlorophenoxyacetic acid (2, 4-D) micropollutant herbicide removing from water using granular and powdered activated carbons: a comparison applied for water treatment and health safety. *J. Env. Sci. Health, Part B*, 55(4): 361-375.
  29. Gülen, J. & Aslan, S. (2020). Adsorption of 2, 4-Di-chlorophenoxyacetic Acid from Aqueous Solution Using Carbonized Chest Nut as Low Cost Adsorbent: Kinetic and Thermodynamic. *Zeitschrift für Physikalische Chemie*, 234 (3): 461-484.
  30. Hoijang, S., Nonkumwong, J., Singhana, B., Wangkarn, S., Ananta, S. & Srisombat, L. (2020). Adsorption of 2, 4-Dichlorophenoxyacetic acid by Magnesium Ferrite Magnetic Nanoparticles Modified with Amine Functional Groups. *Chiang Mai J. Sci.*, 47 (1): 137-146.
  31. Kulaishin, S. A., Vedenyapina, M. D., Sharifullina, L. R. & Lapidus, A. L. (2020). Adsorption of 2, 4-Di-chlorophenoxyacetic Acid on Granular Activated Carbon. *Solid Fuel Chem.*, 54 (1): 54-60.
  32. Lin, C., Qiu, Y., Fan, J., Wang, M., Ye, L., Liu, Y., Yea, X., Huangb, X., Lv, Y. & Liu, M. (2020). Fabrication of photo-responsive cellulose based intelligent imprinted material and selective adsorption on typical pesticide residue. *Chem. Eng. J.*, 394, 124841.
  33. Febrianto, J., Kosasih, A.N., Sunarso, J., Ju, Y.H., Indrawati, N., Ismadji, S. (2009). Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. *J. Hazard. Mater.*, 162: 616-645.
  34. Kim, S. J., Shim, W. G., Kim, T. Y., Moon, H., Kim, S. J. & Cho, S. Y. (2002). Adsorption equilibrium characteristics of 2, 4-dichlorophenoxyacetic acid and 2, 4-dinitrophenol on granular activated carbons. *Korean J. Chem. Eng.*, 19 (6): 967-977.
  35. Njoku V. O., Foo K. Y. & Hameed B. H. (2013) Microwave-assisted preparation of pumpkin seed hull activated carbon and its application for the adsorptive removal of 2,4-dichlorophenoxyacetic acid. *Chem. Eng. J.*, 215-216: 383-388.
  36. Li, S., Feng, F., Chen, S., Zhang, X., Liang, Y. & Shan, S. (2020). Preparation of UiO-66-NH<sub>2</sub> and UiO-66-NH<sub>2</sub>/sponge for adsorption of 2, 4-dichlorophenoxyacetic acid in water. *Ecotox. Environmental Saf.*, 194, 110440.
  37. Xu, S., Yin, Y., Wang, Y., Li, X., Hu, Z. & Wang, R. (2020). Amphoteric superabsorbent polymer based on waste collagen as loading media and safer release systems for herbicide 2, 4-D. *J. Appl. Pol. Sci.*, 137(12): 48480.
  38. Moreira-González, A. (2013). Inusual arribazón de *Sargassum fluitans* (Børgesen) Børgesen en la costa centro-sur de Cuba. *Rev. Invest. Mar.* 33(2): 17-20.
  39. Smetacek, V. & Zingone, A. (2013). Green and golden seaweed tides on the rise. *Nature*, 504: 84-88.
  40. Milledge, J.J. & Harvey, P. (2016). Golden tides: Problem or golden opportunity? The valorisation of sargassum from beach inundations. *J. Mar. Sci. Eng.*, 4: 60.
  41. Burrows, R., Wabnitz, C., Eyzaguirre, J. The Great Sargassum Disaster of 2018. Available online: <https://essa.com/the-great-sargassum-disaster-of-2018/> (accessed on 25 March 2019).
  42. Langin, K. (2018). Seaweed masses assault caribbean islands. *Sci.*, 360, 1157-1158.
  43. Thompson, T.M., Young, B. R. & Baroutian, S. (2020). Pelagic sargassum for energy and fertilizer production in the Caribbean: a case study on Barbados. *Renewable Sust. Ener. Rev.*, 118, 109564.
  44. Liranzo-Gómez, R., García-Cortés, D., Jauregui-Haza, U.. Adaptation and sustainable management of massive influx of sargassum in the Caribbean. *Procedia Env. Sci., Eng. Manag.*, 8(2), 543-553, 2021.
  45. Muñoz Bautista, A. (2013). Composición taxonómica y abundancia de la macrofauna asociada a *Sargassum* (Phaeophyceae: Fucales) flotante en el

- sistema arrecifal veracruzano, suroeste del golfo de México. Universidad Veracruzana. Tesis para obtener el grado académico de: Maestra en Ecología y Pesquerías. 60 p.
46. Dreckmann, K. M. & Sentíes, A. (2013). Las arribazones de algas marinas en el caribe mexicano: evento biológico natural o basura en las playas. *Biodiversitas*, 107:7-11
  47. Hernández-Almaraz, P. (2015). Bioacumulación de Cd, Pb, Cu, Zn y Fe en un gasterópodo y dos especies de erizo por consumo de macroalgas asociadas a mantos de *Sargassum* spp., en Bahía de la Paz, Baja California del Sur, México. Centro de Investigaciones Biológicas del Noroeste, S. C. Tesis para optar por el grado de Doctor en Ciencias. 119 pag.
  48. Gavio B., Rincón-Díaz M. N. & Santos-Martínez A. (2015). Massive quantities of pelagic *Sargassum* on the shores of San Andrés Island, southwestern Caribbean. *Acta Biol. Colomb.*, 20(1): 239-241.
  49. Willoughby, S. (2015). Sargassum and the Fishing Industry. In Proceedings of the Sargassum Symposium, UWI, Cave Hill, London, UK, 17 August 2015.
  50. Van Tussenbroek, B. I., Hernández Arana, H. A., Rodríguez-Martínez, R. E., Espinoza-Avalos, J., Canizales-Flores, H. M., González-Godoy, C. E., Barba-Santos, M. G., Vega-Zepeda, A. & Collado-Vides, L. (2017). Severe impacts of brown tides caused by *Sargassum* spp. on near-shore caribbean seagrass communities. *Mar. Pollut. Bull.*, 122: 272–281.
  51. Resiere, D., Valentino, R., Nevière, R., Banydeen, R., Gueye, P., Florentin, J., Cabié, A., Lebrun, T., Mégarbane, B., Guerrier, G. et al. (2018). Sargassum seaweed on Caribbean islands: An international public health concern. *Lancet*, 392: 2691.
  52. Jessop, D. (2019). Sargassum a Continuing Challenge for Tourism. In *The Caribbean Council Research & Analysis; The Caribbean Council: London, UK, 2019; Volume 22.*
  53. Esmaeili, A., Ghasemi, S., & Sohrabipour, J. (2010). Biosorption of copper from wastewater by activated carbon preparation from alga *Sargassum* sp. *Nat. Prod. Res.*, 24(4): 341-348.
  54. Ibrahim, W. M. (2016). New trend for removing toxic heavy metals from drinking water by activated carbon based brown algae. *Biotech.*, 15 (3-4): 65-75.
  55. Liu, Z., Adewuyi, Y. G., Shi, S., Chen, H., Li, Y., Liu, D. & Liu, Y. (2019). Removal of gaseous Hg0 using novel seaweed biomass-based activated carbon. *Chem. Eng. J.*, 366: 41-49.
  56. Zeng, G., Hong, C., Zhang, Y., You, H., Shi, W., Du, M., ... & Chen, B. (2020). Adsorptive removal of Cr (VI) by *Sargassum horneri*-based activated carbon coated with chitosan. *Water Air Soil Poll.*, 231(2): 77.
  57. Zeng, G., Lou, S., Ying, H., Wu, X., Dou, X., Ai, N. & Wang, J. (2018). Preparation of microporous carbon from *Sargassum horneri* by hydrothermal carbonization and KOH activation for CO<sub>2</sub> capture. *J. Chem.*, 2018, 4319149.
  58. Ding, S. & Liu, Y. (2020). Adsorption of CO<sub>2</sub> from flue gas by novel seaweed-based KOH-activated porous biochars. *Fuel*, 260: 116382.
  59. Ma, M., Ying, H., Cao, F., Wang, Q. & Ai, N. (2020). Adsorption of Congo red on mesoporous activated carbon prepared by CO<sub>2</sub> physical activation. *Chin. J. Chem. Eng.*, 28(4): 1069-1076.
  60. Yeganeh, G., Ramavandi, B., Esmaeili, H. & Tamjidi, S. (2019). Dataset of the aqueous solution and petrochemical wastewater treatment containing ammonia using low cost and efficient bio-adsorbents. *Data in Brief*, 26, 104308.
  61. Francoeur, M., Ferino-Pérez, A., Yacou, C., Jean-Marius, C., Emmanuel, E., Chérémond, Y., Jauregui-Haza, U., Gaspard, S. Activated carbon synthesized from *Sargassum* (sp) for adsorption of caffeine: Understanding the adsorption mechanism using molecular modeling. *J. Envi. Chem. Eng.* 9, 104795, 2021. <https://doi.org/10.1016/j.jece.2020.104795>.
  62. Brunauer, S., Emmett, P. H. & Teller, E. (1938). Adsorption of gases in multimolecular layers,
  63. Quesada-Peñate I., Julcour-Lebigue C., Jáuregui-Hazac U., Wilhelm A. M. & Delmas H. (2009). Comparative adsorption of levodopa from aqueous solution on different activated carbons. *Chem. Engin. J.*, 152:183–188.
  64. Boehm, H. P. (1994). Some Aspects of the Surface Chemistry of Carbon Blacks and Other Carbons. *Carbon*, 32(5): 759–69.
  65. Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (9): 1361–1403.
  66. Jovanović, D. S. (1969). Physical adsorption of gases. *Kolloid-Zeitschrift und Zeitschrift für Polymere*, 235(1), 1214-1225.
  67. Fowler, R. H. (1939). *Statistical Thermodynamics*, Cambridge University Press, Cambridge.
  68. Freundlich, H. (1906). Over the adsorption in solution, *Z. Phys. Chem.* 57: 384–470.
  69. Quiñones, I., & Guiochon, G. (1996). Derivation and application of a Jovanovic–Freundlich isotherm model for single-component adsorption on heterogeneous surfaces. *J. Colloid Interf. Sci.*, 183(1): 57-67.
  70. Quiñones, I., & Guiochon, G. (1998). Extension of a Jovanovic–Freundlich isotherm model to multi-component adsorption on heterogeneous surfaces. *J. Chromat. A*, 796(1): 15-40.
  71. Ruthven, D. M. (1984). *Principles of Adsorption and Adsorption Processes*, Wiley-Interscience, New York, NY.
  72. Akaike, H. (1974). A newlook at the statistical model identification, *IEEE Trans. Autom. Control* 19 (6): 716–723.
  73. Moreno-Castilla, C. (2004). Adsorption of organic molecules from aqueous solutions on carbon materials. *Carbon*, 42 (1): 83–94.
  74. Enriquez-Victorero, C., Hernández-Valdés, D., Montero-Alejo, A. L., Durimel, A., Gaspard, S., & Jáuregui-Haza, U. (2014). Theoretical study of  $\gamma$ -hexachlorocyclohexane and



- $\beta$ -hexachlorocyclohexane isomers interaction with surface groups of activated carbon model. *J. Mol. Graph. Model.*, 51: 137-148.
75. Gamboa-Carballo, J. J., Melchor-Rodríguez, K., Hernández-Valdés, D., Enriquez-Victorero, C., Montero-Alejo, A. L., Gaspard, S. & Jáuregui-Haza, U. J. (2016). Theoretical study of chlordecone and surface groups interaction in an activated carbon model under acidic and neutral conditions. *J. Mol. Graph. Model.*, 65: 83-93.
76. Paredes-Laverde, M., Salamanca, M., Silva-Agredo, J., Manrique-Losada, L. & Torres-Palma, R. A. (2019). Selective removal of acetaminophen in urine with activated carbons from rice (*Oryza sativa*) and coffee (*Coffea arabica*) husk: Effect of activating agent, activation temperature and analysis of physical-chemical interactions. *Journal of Environmental Chemical Engineering*, 7(5): 103318. *J. Am. Chem. Soc.*, 60: 309–319.