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Abstract

Adsorption modeling via statistical physicstheoryallows to understand the adsorption mechanism of heavy metal ions.Therefore, this paper reports the analysis of the mechanism of copperion (Cu^{2+}) adsorption on four activated carbons using statistical physics models. These

models contain parameters that were utilized to provide new insights into the possible adsorption mechanism at the molecular scale. In particular, a monolayer adsorption model was the best alternative to correlate the Cu^{2+}adsorption dataat 25 – 55 °C and pH 5.5. Furthermore, the application of this model for copper adsorption data analysisshowed that the removal of this heavy metal ion was a multi-cationic process. This theoretical finding indicated that Cu^{2+} ions interacted via one functional group of activated carbon surface during adsorption. In this direction, the adsorption energy was calculated thus showing that Cu^{2+}removalwas endothermic and associated with physical interaction forces.Furthermore, theseactivated carbons showed saturationadsorption capacities from 54.6 to 87.0 mg/g for Cu^{2+} removal, and their performances outperformedother adsorbents available in the literature. Overall, these results providenewinsights of the adsorption mechanism of this water pollutantusing activated carbons.

***Keywords**:* Adsorption; Cooper; Isotherms; Statistical physics;

1. Introduction

Copper is a transition metal, electrically and thermally conductive, but it is also consideredas an environmental pollutant(Kayalvizhi et al. 2022). Natural disasters (e.g., volcanicphenomena) and anthropogenic activities (e.g., metal industries, tanning factories, and automobile industries) contribute to the pollution caused by copper.This metal is toxic even at relatively low concentrations, and, consequently, the highest permissible concentration level of copper ions(Cu^{2+}) in marine waterhas been established as4.8 μg/L. In comparison, the maximum Cu^{2+} concentration for drinking water is 1300 μg/L,as reported by the WHO and EPA(Katiyar et al. 2021; Kayalvizhi et al. 2022). Chronic exposure to this metal can affect vital organs such as the

intestines, stomach, and liver. It can also generate diverse symptoms such as liver disease, gallbladder, and metabolic disturbances(Dou et al. 2019; Sun et al. 2022).

Consequently, the drinking water resources and effluents polluted with Cu^{2+} must be treated to reduce their concentration thus avoiding environmental impacts and to protect human health. Various procedures have been reported to remove Cu^{2+} ions from liquid phase. They includeion exchange, precipitation, electrolysis, reverse osmosis, flocculation, biochemical methods, and membrane-based filtration (Godiya et al. 2019; Nyström et al. 2020; Anbazhagan et al. 2021; Lemes and Tarley 2021). However, these removal methods have disadvantages such as unfavorable cost-effectiveness tradeoffsor the generation of toxic sediments and wastes(e.g., sludge)(Rukayat et al. 2021). In contrast, the adsorption process is a competitive technique compared to other methods due to its ease of handling, low cost, and removal efficacy even at low concentrations of heavy metal ions (Vocciante et al. 2014; Pan et al. 2019; Khan et al. 2021).Activated carbon is the most employed adsorbent in this processbecause it effectively removesinorganic and organic pollutants from wastewaters and industrial effluents.This adsorbent outperforms other materials reported for water treatment in terms of itsproduction cost and the availability of a wide spectrum of preparation routes that is already exploited and commercialized at large industrial scale. The adsorption performance of activated carbon is governed by its pore structure and surface chemistry. The modification of activated carbon is aimed to optimize these properties (Bell et al. 2011), and this adsorbent can be obtained from different feedstock and preparation conditions, thus affecting its adsorption properties.Surface functionalization of activated carbons can be performed with several chemicals to tailor their performance for the removal of target pollutants.

Under this context, citric wastes can be an option to produce activated carbons since they are generated in large amounts by industries of juices and jams. During the production process of juices and jams, around 50-60% of the entire citric fruit is discarded. These wastes

cannot be released into the environment since they generate CH_4. On the other hand, they are rich in lignin, cellulose, hemicellulose, and pectin, thus being an attractive feedstock for pyrolysis and their conversion into activated carbon (Lam et al. 2016, 2018).

The modeling of adsorption data of heavy metals and other water pollutants is important for water treatment design. Therefore, it is possible to apply classical models (e.g., Langmuir) to theoretically study the adsorption data. Unfortunately, this and other tradditional modelsare not useful to understand the adsorption mechanims due to the limitations in their hypotheses. For instance, Langmuir modelconsiders that each functional group can accept one ion for all adsorption systems. This assumption is an obstacle to provide proper interpretations of more complex adsorption mechanisms. The application of reliable models to analyze and explain the adsorption of heavy metal ions on activated carbon surfaces is paramount to develop effective and low-cost water treatment methods.

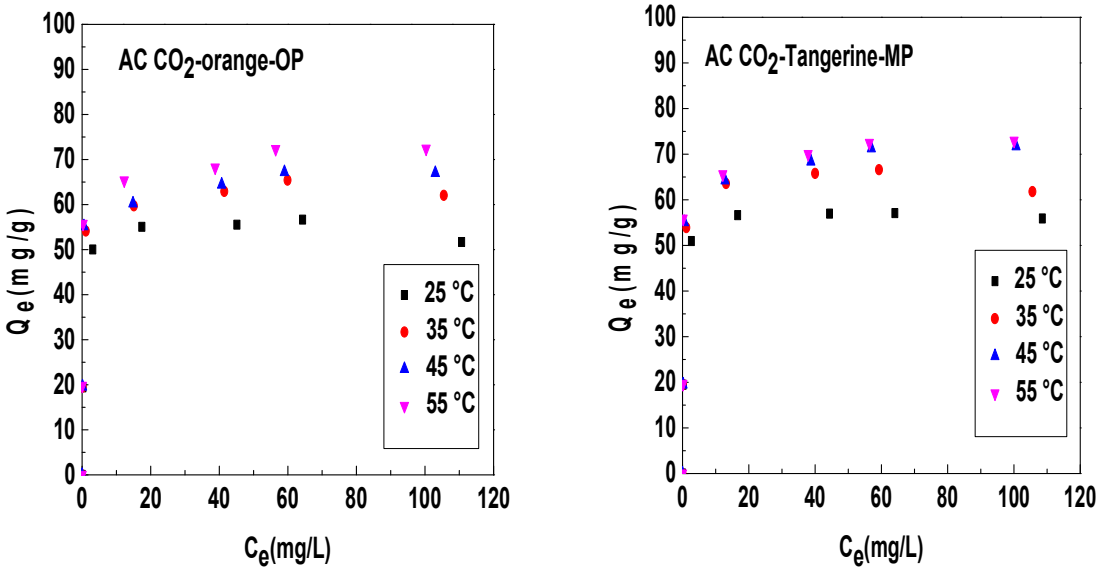
In this research,two homogeneous and heterogeneous models based on statistical physics theory were implemented to explain the adsorption mechanism of Cu^{2+}on a set of activated carbons obtained from different citric wastes namelyorange (OP), tangerine (MP), lemon (RLP) and lime (SLP). These models allowed to analyze the adsorption mechanismat the microscopic scale. New insightson steric and energetic parameters that governed the removal of this relevant water pollutant were developed for all tested activated carbons.

2. Description of experimental isotherms and statistical physics models

2.1. Preparation of AC and quantification of Cu^{2+} adsorption isotherms

Cu^{2+} adsorption isotherms were quantified with four activated carbons prepared from citrus waste(Dotto et al. 2011; Perondi et al. 2017).For the adsorbent preparation, 100 g of each citrus

waste werelocated in a stainless reactor of 127 x 8.5 cm. The reactor was heated at 5 ºC/min until 900 °C and remained at this temperature for 15 min. Then, the system was cooled until ambient temperature. All these steps were performed with N_2 flowof 0.2 L/min. Subsequently, the N_2 flow was replaced by CO_2 flow (2 kg/h for 15 min). Finally, the adsorbent samples were removed from the reactor, washed and used in adsorption experiments. These adsorbents were labelled as AC CO_2-orange-OP, AC CO_2-tangerine-OP,AC CO_2-lemon-RLP and AC CO_2-Lime-SLP.



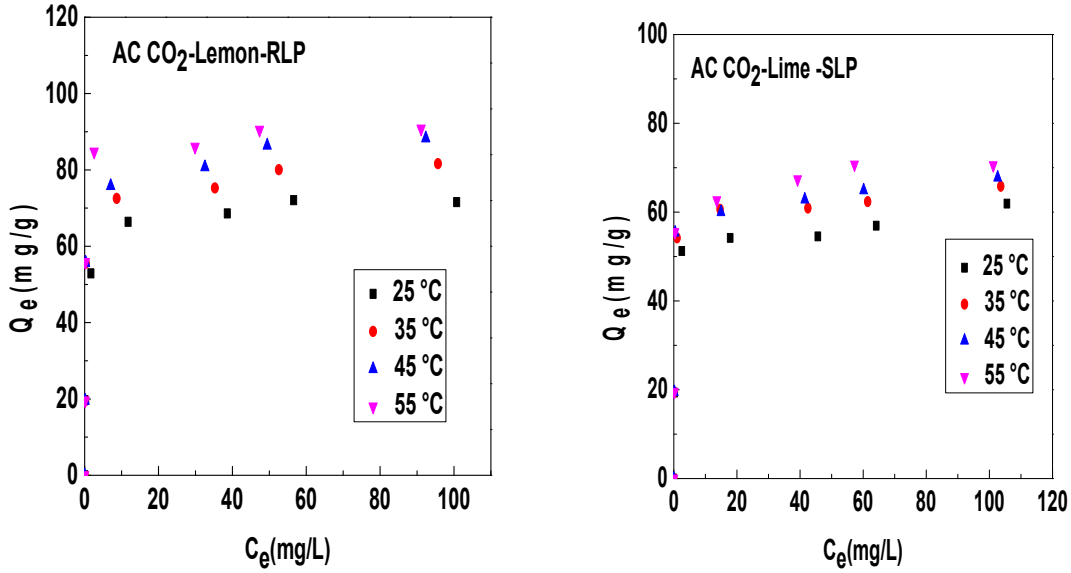


Figure 1: Experimental isotherms of the adsorption of Cu^{2+}ions on different activated carbons at 25-55 °C and pH 5.5.

Typical batch equilibrium experiments were performed to obtain the Cu^{2+} adsorption isotherms. Aqueous solutions (50 mL) with different initial Cu^{2+} concentrations up to 150 mg/L were prepared from copper sulfate and the solution pH was adjusted to 5.5. Next, these solutions were placed in Erlenmeyer flasks located in a thermostated shaker. Adsorption isotherms were quantified at 25, 35, 45 and55 °C using an activated carbon dosage of 0.5 g/L under constant stirring of 200 rpm for 5 h. The solid-liquid separation was performed by centrifugation and Cu^{2+} concentration in the liquid was quantified by flame atomic absorption spectroscopy.Then,the equilibrium adsorption capacities were calculated via a mass balance for a stirred tank using the initial and final Cu^{2+} concentrations used in the experiments and the corresponding adsorbent dosage. Figure 1 shows the experimental isotherms of Cu^{2+}adsorptionon the four activated carbons analyzed in this paper.

Solution temperature positively affected all adsorbed quantities of Cu^{2+}ions on these activated carbons, thus suggesting an endothermic removal process. All experimental isotherms followed the monotonic trend of adsorbed Cu^{2+} quantities as a function of equilibrium concentration until the saturation region was reached. This adsorbent saturation was caused by forming a layer of Cu^{2+}ions adsorbed on the surfaces of tested activated carbons. In this regard,homogeneous and heterogeneous monolayer models developed from statistical physics theory were implemented to analyze Cu^{2+} adsorption isotherms at the microscopic scale. The next two scenarios were tested in this modeling study:

Scenario1:A homogeneous monolayer model (HMM) was considered where only one type of functional groupparticipated in the adsorption of Cu^{2+} ions on tested adsorbents. It was assumed that only one adsorption energy was involved in the metal ion removal, which represented the

interaction ofCu^{2+} ion–activated carbon surface. The adsorbed quantity calculated with this model is given by (Sellaoui et al. 2018; Dhaouadi et al. 2020c, b, a):

$$Q_e = \frac{nS_m}{1+\left(\frac{C_{1/2}}{C_e}\right)^n} \quad (1)$$

Scenario 2: A heterogeneous monolayer model (IMM) was also applied. Two functional groups participated in the adsorption of Cu^{2+} ions with two different adsorption energies: Cu^{2+} ion – adsorption site 1 and Cu^{2+}ion– adsorption site 2. In this model, the adsorbed quantity as a function of the equilibrium concentration isdefined as (Dhaouadi et al. 2020b, a, 2021):

$$Q_e = \frac{n_1 S_{m1}}{1+\left(\frac{C_1}{C_e}\right)^{n_1}} + \frac{n_2 S_{m2}}{1+\left(\frac{C_2}{C_e}\right)^{n_2}} \quad (2)$$

For these models, n and n_i(i=1, 2) are the numbers of Cu^{2+} ions adsorbedper functional group(s), S_m and $S_{mi}$are the densities of these surface functionalities, $C_{1/2}$and C_i(i=1, 2) are the concentrations at half-saturation, respectively.

Characterization results showed that these activated carbons contained different functional groups that can contribute to the adsorption of Cu^{2+}ions. Therefore, these adsorption models were consistent with the surface chemistry of these activated carbons.Note that thesemodels were developed by applying a grand canonical ensemble of statistical physics with the aim of obtaining a better analysis of the adsorption mechanism of this pollutant. Overall, these models assumed that the adsorption of Cu^{2+}ions was a monolayer process, but with the contribution of one (homogeneous monolayer model) and two (heterogeneous monolayer

model) functional groups in the removal of this cation(Dhaouadi et al. 2020b, 2021).In summary, these models can describe the role of these functional groups on the adsorption of this metallic ion andcan also characterize the nature of their interactions (i.e., multi-interaction or multi-ionic process).

Table 1: Results of the Cu^{2+}adsorption isothermcorrelation with a homogeneous monolayer model.

T(°C)	R^2	n	S_m (mg/g)	$C_{1/2}$(mg/L)	Q_s (mg/g)
		AC CO_2- Orange–OP			
25	0.992	1.13	48.35	0.38	54.63
35	0.994	1.46	42.61	0.31	62.21
45	0.989	1.70	37.88	0.19	64.39
55	0.977	1.82	37.49	0.07	68.23
		AC CO_2- Tangerine–MP			

25	0.999	1.07	53.20	0.35	56.92
35	0.995	1.24	51.80	0.32	64.23
45	0.989	1.83	37.65	0.27	68.89
55	0.990	4.20	16.71	0.14	70.18
	AC CO_2- Lemon-RLP				
25	0.998	0.63	115.75	0.39	72.92
35	0.987	2.88	26.85	0.25	77.32
45	0.984	2.90	28.55	0.22	82.79
55	0.994	4.55	19.32	0.18	87.90
	AC CO_2-Lime-SLP				
25	0.984	1.15	49.55	0.44	56.98
35	0.993	1.56	40.03	0.31	62.44
45	0.988	3.04	20.96	0.238	63.71
55	0.988	3.16	21.42	0.232	67.68

These models were employed to fit all Cu^{2+} ion adsorption isotherms, and their parameters were determinedvia a multivariable nonlinear regression with the Levenberg-Marquardt method. Determination coefficients(R^2) and the trends of steric and energetic parametersindicated that the HMM model was the most suitable for analyzing the Cu^{2+} removal at the microscopic scale. Table 1 provides the results of Cu^{2+} adsorption data fitting for the HMM model and their corresponding steric and energetic parameters fortested experimental conditions. In addition, the fitting of Cu^{2+}adsorption isotherms by the HMM model is illustrated in the appendix.

3. Results and discussion

3.1. Evaluation of the number of Cu^{2+} ions adsorbed per functional group and their adsorption site densities

The impact of temperature on the number of adsorbed Cu^{2+} ions per functional group and their corresponding adsorption site densities for these activated carbons is represented in Figure 2.

Allparameters *n*werehigher than unity except for AC CO_2-Lemon-RLP adsorbent at 25 °C. This result indicated that the adsorption of this heavy metalwas multi-cationic for these activated carbons, where the functional groups could adsorb several cations simultaneously(Dhaouadi et al. 2020b, a). Indeed, the exceptional case (i.e., n=0.63) showed that Cu^{2+} ions could be adsorbed on the surface of AC CO_2- Lemon-RLP via a combined interaction where one and two functional groups can participate in the removal with two different proportions(Dhaouadi et al. 2021). Thermally speaking, the temperature increasedthe number of Cu^{2+} ions adsorbed per functional group from 1.13 to 1.82, 1.07 to 4.20, 0.63 to 4.59, and 1.15 to 3.16 for the adsorbents AC CO_2-Orange-OP, AC CO_2-Tangerine-MP, AC CO_2-Lemon-RLP and AC CO_2-Lime-SLP, respectively. Overall, these results indicated that the temperature played a relevant role to adsorb theCu^{2+}ions.

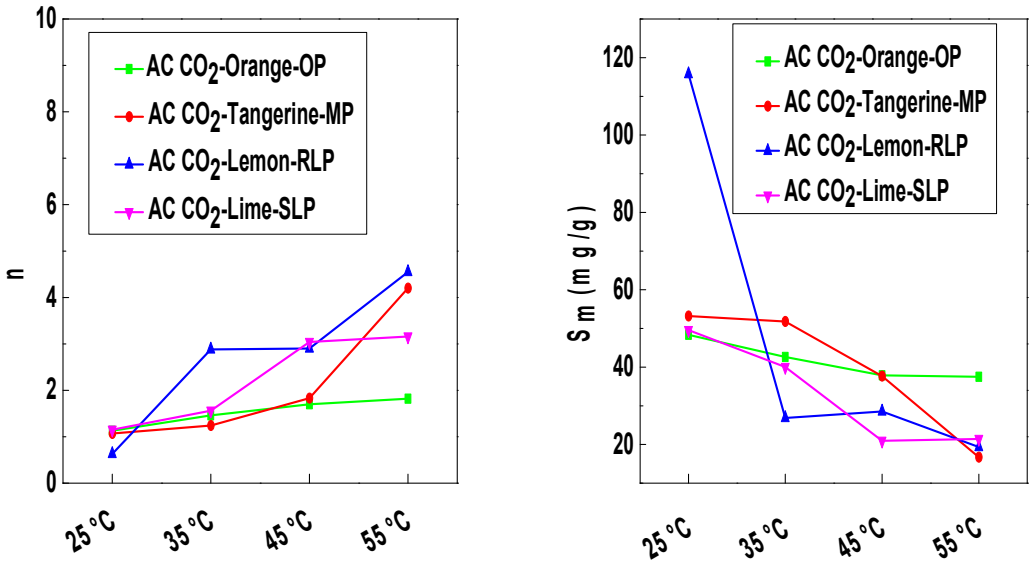


Figure 2: Impact of temperature on the parameters n and S_m for theCu^{2+}adsorption at pH 5.5 using different activated carbons.

Figure 2 indicated that the density of functional groups of these activated carbons reduced as a function of temperature. Moreover, this tendency was inversely proportional to the number of Cu^{2+} ions adsorbed per functional group. Thus, theincrement of the parameter n as a function of temperature suggested a reduction of the occupied functional groups and, consequently, a decrement of the adsorption density and vice versa.

3.2. Performance evaluation of different activated carbons for Cu^{2+} adsorption

The performance of tested adsorbents was complemented via the calculation of adsorption capacities at saturation using the next expression:

$$Q_s = nS_m \quad (3)$$

The impact of thermal agitation on the adsorbed quantity at saturation Q_s for the different adsorbents is given in Figure 3.

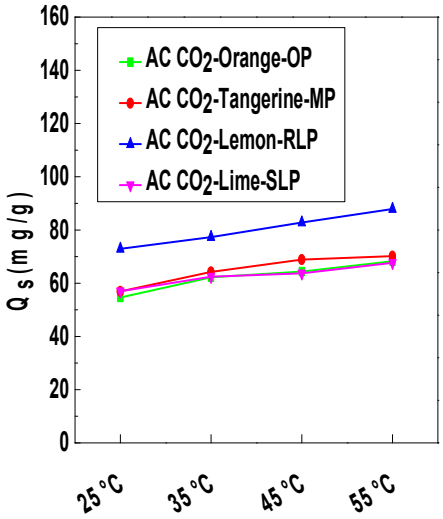


Figure 3: The adsorbed quantity of Cu^{2+}ionsat saturation as a function of temperature for different activated carbons at pH 5.5.

Figure 3 indicated that the adsorbed quantity at saturation for the four activated carbons increased with the solution temperature. This result confirmed that the solution temperature enhanced the mass transfer phenomena and the diffusion of Cu^{2+} ions inside the porous structure of these adsorbents. Thus, the increment of this quantitywas associated with the number of adsorbed ions per functional group and the adsorption energy. Comparatively, the AC CO_2-Lemon-RLP adsorbent showed the highest Cu^{2+}removal and was the most effective for this purpose. Furthermore, characterization results reported in (Dotto et al. 2011) indicated that theacidic functionalities of theseactivated carbonswere responsible forCu^{2+} removal.In particular, FTIR analysis of activated carbon samples before and after Cu^{2+} adsorption indicated that the main acidic functional groups were OH and COOH. The absorption bands relative to these groups presented significant shifts after Cu^{2+} adsorption thussuggesting that OH and COOH were involved in the interactions with Cu^{2+} ions, and confirming the statistical physics calculations.

For illustration, Table 2 shows the Cu^{2+} adsorption capacities for different activated carbons reported in the literature.It was clear that these activated carbons can be an alternative to remove the Cu^{2+} ions from wastewatersand to contribute to the reduction of solid waste generation. They can also outperform other adsorbents reported in the literature. For instance, the Cu^{2+}adsorption capacities of 1-iron-modified flaxseed waste, sodium dodecyl sulfate modified iron pillared montmorillonite, and activated carbons functionalized with magnetic iron oxide nanoparticles were 7.64, 20.6, and 41.6 mg/g(Li and Wu 2010; Gu et al. 2019; Cerrahoğlu Kaçakgil and Çetintaş 2021).

Table 2. Cu^{2+}adsorption capacities of activated carbons obtained from different feedstock(Mariana et al. 2021).

	Preparation conditions		
Feedstock	Temperature, °C	Time, min	Adsorption capacity, mg/g
Cauliflower leaves	600	120	75.99
Gingko leaf	800	90	310.0
Pinewood sawdust	700	120	419.1

3.3. Cu^{2+} adsorption energy

Adsorption energy for the interaction Cu^{2+} ion-activated carbon surface was determined from the concentration values at half-saturation and the following equation (Dhaouadi et al. 2021):

$$\Delta E_{int(FG-Cu^{2+})} = RT \ln \frac{C_s}{C_{1/2}} \qquad (4)$$

where$R$=8.314 J/mol·K is the ideal gas constant, and C_s is the copper solubility.Theadsorption energy for the interaction of acidic functional groups ofthese activated carbonsand Cu^{2+} ions is depicted in Figure 4.

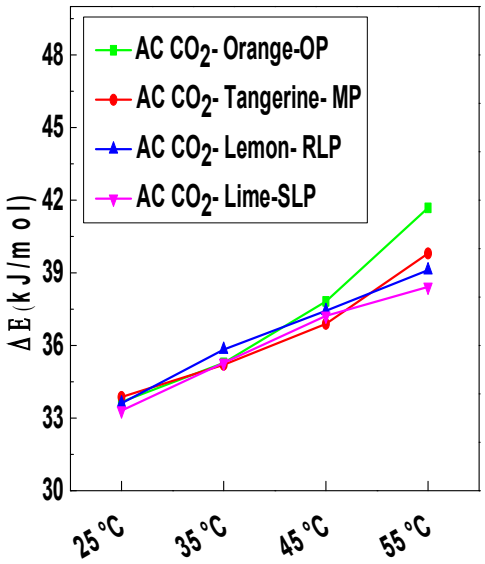


Figure 4: CalculatedCu^{2+} adsorption energies for testedactivated carbons.

All interaction energy values were lower than 40 kJ/mol, thus suggesting that this adsorption process was associated with physical forces. As stated, the acidic functional groups (e.g., OH and COOH) of these activated carbons were involved in the Cu^{2+} adsorption. Furthermore, this adsorption energy increased with solution temperature for all activated carbons.

4. Conclusions

A reliable modeling of adsorption data and the corresponding analysis of adsorption mechanism are paramount for the design of water treatment processeseffective to remove heavy

metals with activated carbons. Therefore, this study reports the statistical physics-based interpretation of Cu^{2+} adsorption using four activated carbons obtained from citrus wastes, which are low-cost feedstock to prepare new adsorbents.Steric and energetic parameters were calculated for the adsorption of this heavy metal using a monolayer adsorption model. Results showed that the Cu^{2+} adsorption was multi-cationic via one functional group (i.e., acidic surface functionalities). In addition, Cu^{2+} adsorption was endothermic and associated with physical interaction forces. At saturation, Cu^{2+} adsorption capacities ranged from 54.6 to 87.9 mg/g for these activated carbons. Finally, this advanced modeling provided interesting interpretations of the adsorption mechanism of this relevant water pollutant with low-cost activated carbons.

Acknowledgements

Sonia Taamalli, Florent Louis, and Abderrahman El Bakali appreciated the support from the LABEX CaPPA (Chemical and Physical Properties of the Atmosphere), which is funded by the French National Research Agency (ANR) through the PIA (Programmed'Investissementd'Avenir) under contract ANR-11-LABX-0005-01 and also the Regional Council "Hauts de France" and the "European Funds for Regional Economic Development.

-**Ethical Approval**: Not applicable

-**Consent to Participate**: Not applicable.

-Consent to Publish: Not applicable.

-**Author Contributions**: **Conceptualization**: LotfiSellaoui, Abdemottaleb Ben Lamine, **Methodolog**: Kátia da BoitMartinello, Fatma Dhaouadi , Michael Badawi, Adrián Bonilla-Petriciolet, Luis Felipe Oliveira Silva, Guilherme Luiz Dotto, SoniaTaamalli

Writing - original draft preparation: LotfiSellaoui, Fatma Dhaouadi, Florent Louis, Abderrahman El Bakali

Supervision: LotfiSellaoui

-**Funding**: Not applicable

-**Competing Interests**: The authors declare that they have no competing interests

-**Availability of data and materials**: Note applicable

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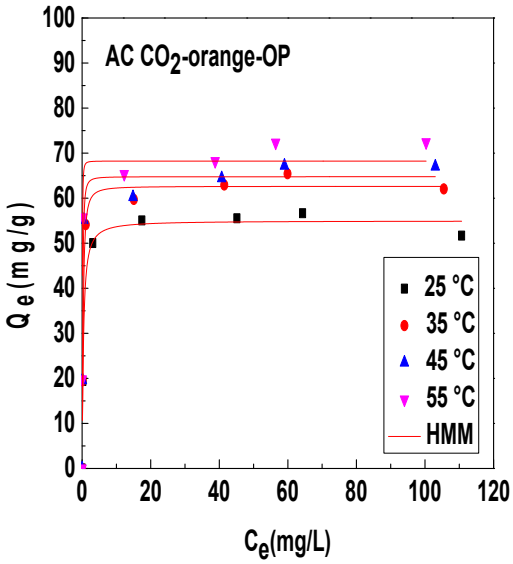
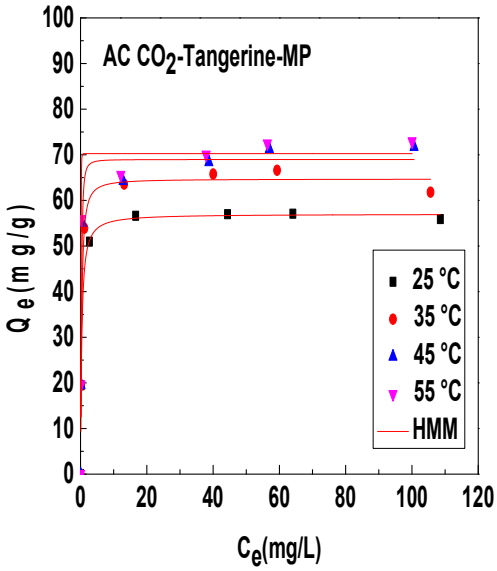
411 **Appendix**

412 The fitting data results of the experimental isotherms of Cu^{2+}ions are given below:





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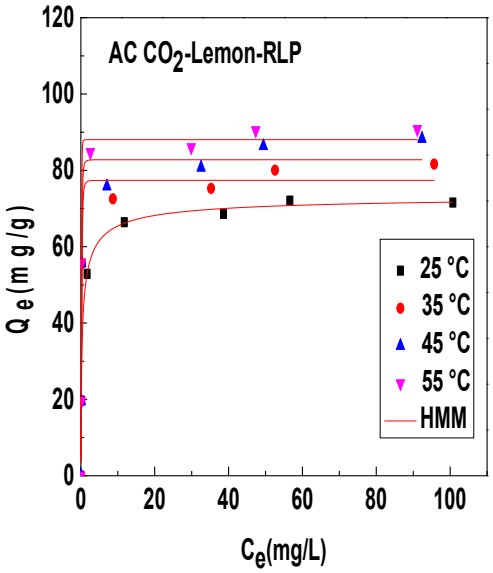

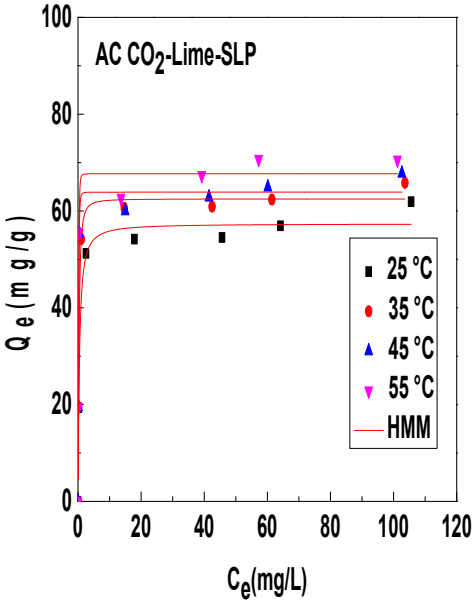

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