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Title: Preparation of activated carbon from kenaf by activation with H₃PO₄. Kinetic study of the adsorption/electro-adsorption using a system of supports designed in 3D, for environmental applications

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CONFLICT OF INTEREST FORM

Manuscript title: *Preparation of activated carbon from kenaf by activation with H_3PO_4 . Kinetic study of the adsorption/electroadsorption using a system of supports designed in 3D, for environmental applications.*

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Best regards,

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May 31, 2019

General Editor
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CHEMICAL ENGINEERING**

RESPONSE TO REVIEWERS:

Dear Editor,

We appreciate the comments made, as they suppose contributions that undoubtedly, clarify and greatly improve the text and interest of this article.

I attach the entire revised article, indicating in blue the contributions and changes for the manuscript entitled: "*Preparation of activated carbon from kenaf by activation with H_3PO_4 . Kinetic study of the adsorption/electro-adsorption using a system of supports designed in 3D, for environmental applications*".

Reviewer 1:

1.- I don't understand "word Kaolin" in the highlights.

Corrected. The word Kaolin has been deleted.

2.- More detailed information should be included in the methodology. It is necessary to know what conditions were used to perform the kinetic and equilibrium tests.

Added to article. The methodology has been expanded and improved.

3.- High concentrations (85%) of acid may not be friendly to the environment, that contradicts the introduction.

More detail and explanation has been included in the article.

In line 92, the following paragraph is inserted which explains how to avoid the polluting effect of excess phosphoric acid: "The phosphoric acid used and existing in the washing water is recovered and reused."



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4.- Adsorption isotherms and their respective analysis must be added to complement porosity information.

Nitrogen adsorption isotherms have not been added, because the objective was only to determine the textural parameters porosity and specific surface and to analyze their influence in the adsorption and electroadsorption process. As well as, not to make too extensive the article.

5.- The copper adsorption values are very low compared with the bibliography. Which is the reason?

The reason is first in this article only analyzes the kinetics of the processes of adsorption and electroadsorption and not the adsorption of the prepared samples. Second, the bibliography contains data on adsorption and electroadsorption of activated carbons that have been chemically modified, as we have done in another article, or the experimental conditions are substantially different.

Reviewer 2:

1.- In conclusion section, authors pointed out that the adsorption/electroadsorption kinetics obeyed the pseudo-second order and therefore copper is chemisorbed on the surface of the activated carbons. At the same time, they mentioned that intraparticle diffusion may not be the only mechanism that influenced the adsorption rate of ions on the adsorbent due to the presence of multiple linear stages in the profile. Which is the rate-determining step?

The mechanism of intraparticle diffusion has been better explained, for which the following text has been introduced:

“Intraparticle diffusion plots have two stages. The first stage is due to an instantaneous adsorption or adsorption on the outer surface, where the adsorbate travels to the outer surface of the adsorbent. In the second stage a gradual adsorption occurs where the intraparticle diffusion is the velocity limiting, i.e., the adsorbate travels within the pores of the adsorbent.”

2. The highest copper retention capacity was observed with P-60-500. It is due to the large mesopore volume. Interestingly, the electrical conductivity of P-60-500 shows large value compared with the other active carbons as shown in Fig. 4. How is it explained?

The increased electrical conductivity of the P-60-500 sample may be due to the existence of graphical structures, aromatic rings, oxygen groups, etc., which allows a higher level of mobility to be produced in the electrons or, in other words: a much higher degree of electricity transfer is produced.

And it is possible to say that in the supposed of the graph, the carbon atoms make up a series of hexagonal rings that are located in a single flat space that in turn makes up a set of sheets that remain joined by the mutual attraction that they generate themselves.

So, if you make an observation of these hexagonal rings is that you can check why the graphite conducts electricity. By making such an observation it can be understood that in said rings there is a double bond that enables the migration of electrons.

In addition to all the above, the carbons take in their bosom a flat hybridization, which allows to conform, as already mentioned, a conjunction of sheets that overlap. To put an analogy to what is being said we could say that these sheets are created in the same way as a hive, parallel to each other and with links from different planes that have a higher level of weakness, this structure allows a higher level to be produced of mobility in electrons or, put another way: there is a much higher degree of electricity transfer.

3. What kind of the copper salt was used? In Experimental section, the following sentence is found: The Cu (II) ion concentration was measured with the aid of a Perkin Elmer flame atomic absorption spectrometer. Does the counter ion species affect the adsorption behavior? Further, the initial concentration of Cu (II) ion should be added in



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the adsorption experiment (It is difficult to find the initial concentration from the plots of Fig.5).

It has been specified in the article.

The salt used CuSO_4

Initial concentration $25 \text{ mg}\cdot\text{L}^{-1}$

There is competition between the acidic and basic active centres of activated carbon to retain both the SO_4 anion and Cu^{2+} . In this work we are only interested in determining the concentration of adsorbed Cu^{2+} . In the case of a covalent adsorbate, the molecule is normally polarised and adsorbed on the active centres of the activated carbon.

4. Incomplete description of Ref. is seen for [21], [25], [27] and [28].

It has been corrected and completed in the article.

I look forward to hearing from you soon.

Best regards,

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HIGHLIGHTS:

- Activated carbons were obtained from kenaf and were activated by H_3PO_4 , materials suitable for adsorption of harmful substances to humans and environment.
- Although the non-electroadsorption can be doped to increase its capacity of electroadsorption, opening a new line of research not collected in the literature.
- In this manuscript is used elements designed in 3D that facilitate this process of adsorption and opens a new path for new 3D designs for adsorption / electroadsorption.

1 **Preparation of activated carbon from kenaf by activation with H₃PO₄.**
2 **Kinetic study of the adsorption/electroadsorption using a system of**
3 **supports designed in 3D, for environmental applications**

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12 **Abstract**

13 Activated carbons were prepared from kenaf by chemical activation with phosphoric
14 acid in different concentrations. Its electrical conductivity was also determined. From
15 the series of prepared activated carbons, those with better textural properties, chemistry
16 and high electrical conductivity were selected for their use in adsorption and
17 electroadsorption processes.

18 The removal of Cu (II) ions from aqueous media is of great interest due to their harmful
19 effects on health and environment. The aim of this work was to study the kinetics in the
20 process of retention of copper ions in aqueous solution by adsorption and
21 electroadsorption using activated carbon. Thus, when comparing both processes it was
22 observed that the adsorption equilibrium times were generally greater than those
23 corresponding to electroadsorption. Different kinetic models were applied. The kinetic
24 models applied to the adsorption/electroadsorption processes indicated that the pseudo-
25 second order model described both processes in a better way than the pseudo-first order
26 model. The values of R² in electroadsorption kinetics were closer to 1 than those
27 obtained in adsorption kinetics. Therefore, it can be affirmed that the pseudo-second
28 order model for the samples, object of study, is better adjusted to the electroadsorption
29 process.

30 **Keywords:** Activated carbon; Adsorption; Electroadsorption; Kinetics model; Copper
31 ion.

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1. Introduction

Activated carbons (ACs) have a crystalline structure of graphitic type that is characterized by high volume of micropores and mesopores, which gives the material a high surface area. However, commercial AC can be regarded as relatively expensive for some applications. Consequently, the use of agricultural biomass waste as a precursor to the manufacture of AC [1–3] emerges as an alternative.

Kenaf is an appropriate material for being used as precursor in the manufacture of AC. It is a dicotyledonous plant, belonging to the genus *Hibiscus* (Malvaceae family). Kenaf is a good source of biomass due to its abundance, since it can grow under a wide range of climatic conditions requiring minimal amounts of water, fertilizers or pesticides. It is also a plant rich in cellulose. The stem of the kenaf plants consists of an outer bark and an inner core, both containing fibrous components that can be used for adsorption [4-5]. In the activation process to obtain an activated carbon, it is necessary to take into account the type of precursor and the activation agents, since the use of different compounds provides an AC with several porous properties and structures [6]. The H_3PO_4 is an activating agent that allows to work at low temperatures (over 400 °C). Furthermore, it does not cause corrosion in the equipment and leaves no metallic residues, which makes it respectful of the environment, and provides AC micro- and mesopores with high surface area [5],[7-8].

Materials with the properties above described are suitable for adsorption of harmful substances to humans and environment [9-10]. Clear examples of these harmful substances are heavy metals that are found in our environment above controlled levels. The term heavy metals is applied to those elements whose atomic weight is between 63.5 and 200.6, and have a specific gravity above 5.0 [3]. These materials are non-biodegradable and have a tendency to be accumulated in living organisms. This is why

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the level of these heavy metals in the environment is increasing day by day. The main sources of these heavy metals are wastewater pollution in industrial processes, metal cleaning, boiler piping, and fertilizer production.

Copper is a heavy metal that is particularly harmful to humans, a long exposure to copper above acceptable concentration levels can result in irritation of nose, mouth and eyes, headaches, nausea, vomiting, diarrhoea and, in extreme cases, can damage the kidneys for life and cause death [9],[11–13].

Electroadsorption is defined as an adsorption phenomenon induced by a potential difference applied on the surface of an electrode [14]. When an external electric field is imposed between two electrodes immersed in an electrolytic solution, the ions are forced to move towards the opposite charge electrodes, this resulting in a separation of charges through the electrode/dissolution interface [15]. This phenomenon can significantly improve the adsorption capacity of activated carbons without the need of impregnation. This is due to the fact that the electronic density of the adsorbent changes with the potential applied, this favouring the interaction with the ionic species in the dissolution [16].

In this work, the study of Cu^{2+} ion adsorption/electroadsorption and its kinetic model was performed using activated carbon. Activated carbons were obtained from kenaf and activated by H_3PO_4 .

2. Experimental.

The materials used have been:

- Kenaf (K), from which activated carbon (AC) has been prepared by chemical activation.
- Carbon black Vulcan 3 (V3), from Cabot Corporation, used to improve the electrical conductivity of the prepared samples.

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83 - Polyvinylidene fluoride (PVDF), powder, provided by Aldrich (Sigma-Aldrich
84 Chem., S.L.) and used in this work as binder for the preparation of activated
85 carbon electrodes.

86 25 g of kenaf were impregnated with 100 ml H₃PO₄ (at concentrations of 36%, 60%,
87 and 85%) at 85 °C during 2h. The solid product was subjected to a heat treatment at
88 different temperatures 350-550 °C, with a heating rate of 5 °C min⁻¹ in a N₂ atmosphere
89 (rate flow of 85 ml·min⁻¹). Isothermal conditions at the selected temperature were
90 maintained during 2 h. Finally, the product was washed using distilled water (neutral
91 pH) and dried at 120 °C. [The phosphoric acid used and existing in the washing water is
92 recovered and reused.](#)

93 The chemical characterization was carried out using two tests: chemical analysis, and
94 surface functional groups analysis. The textural characterization of the samples was
95 performed by nitrogen adsorption and mercury porosimetry. The DC electrical
96 conductivity (S) was measured at room temperature by impedance spectroscopy over
97 the frequency range from 20 to 10⁶ Hz at a voltage of 1V.

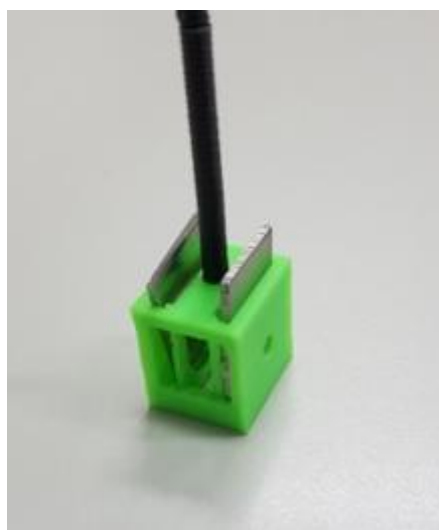
98 The kinetic study of the adsorption process was carried out. For measuring an adapter
99 was designed in three dimensions to be incorporated into a thermostatic bath with
100 agitation (Figure 1). This adapter supported vessels containing carbon samples in
101 contact with Cu (II) ion dissolution. The adapter designed in 3D allows the recipients to
102 be subjected to pressure in each hole and, as a result, to the same agitation speed.



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14 105 **Figure 1. Adapter designed in 3D to be incorporated into a thermostatic bath.**

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16 106 The electrodes to be studied were prepared from various raw materials. These raw
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18 107 materials were Carbon Black (Vulcan 3, V3), Polyvinylidene fluoride (PVDF, supplied
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20 108 by Sigma-Aldrich Chemical S.L.), and activated carbons P-60-450, P-60-500 and P-60-
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22 109 550.

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26 110 The kinetic study of the electroadsorption process was performed in a system of
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28 111 integrated electrodes (designed in 3D) to support cylindrical activated carbon electrodes
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30 112 (Figure 2). This support allows the contact between the cylindrical carbon electrodes
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32 113 and the dissolution of Cu (II) ions.



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54 115 **Figure 2. System of integrated electrodes (designed in 3D).**

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56 116 The advantage of this design (Figure 2) is that it allows, on the one hand, maintaining
57
58 117 the parallelism of the electrodes, which facilitates the process of electroadsorption ,and

118 on the other hand, modifying the distance of separation between the electrodes until
119 reaching the optimal distance.

120 In order to study the adsorption/electroadsorption kinetics, fixed amounts of adsorbent
121 0.1g of activated carbon and volumes of adsorptive solution(80 mL) of a given initial
122 concentration $25 \text{ mg}\cdot\text{L}^{-1}$ of CuSO_4 were kept in contact at constant temperature for a
123 given period of time previously set. With the aim of checking the evolution of the
124 adsorption process with time, the concentration of solute was analysed. The
125 equilibrium time, t_e , may be defined as the minimum period of time that is necessary to
126 keep the value of concentration unvaried.

127 The Cu (II) ion concentration was measured with the aid of a Perkin Elmer flame
128 atomic absorption spectrometer (Model Thermo Corporation). In this study, different
129 kinetic models were tested: pseudo-first order model, pseudo-second order model, and
130 intraparticle diffusion.

132 3. Results and Discussion

133 The interest in the application of carbons as electrodes has increased in recent years
134 [17]. This interest is due to the properties of carbonaceous materials, such as electrical
135 conductivity, specific surface, pore distribution, and easy processibility.

136 In view of the results previously obtained, it is of great importance to study the
137 behaviour of the samples prepared in the process of adsorption/electroadsorption.

138 3.1. Textural characterization

139 **Table 1. Textural parameters of ACs prepared with H_3PO_4 .**

Sample	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	V_{mi} ($\text{cm}^3\cdot\text{g}^{-1}$)	V_{me} ($\text{cm}^3\cdot\text{g}^{-1}$)	$V_{\text{me-p}}$ ($\text{cm}^3\cdot\text{g}^{-1}$)	$V_{\text{ma-p}}$ ($\text{cm}^3\cdot\text{g}^{-1}$)
P- 36- 350	600	0.33	0.11	0.11	0.16
P- 36- 400	799	0.48	0.14	0.14	0.21
P- 36- 450	955	0.54	0.21	0.21	0.22
P- 36- 500	1556	0.88	0.22	0.22	0.25
P- 36- 550	1804	1.02	0.33	0.33	0.25
P- 60- 350	853	0.40	0.17	0.25	0.28
P- 60- 400	1255	0.50	0.40	0.29	0.34
P- 60- 450	1567	0.62	0.65	0.35	0.34

P-60-500	2270	0.88	1.15	0.35	0.42
P-60-550	2145	0.98	0.63	0.40	0.43
P- 85- 350	955	0.54	0.67	0.63	0.32
P-85-400	1208	0.68	0.76	0.60	0.44
P- 85- 450	1496	0.84	0.86	0.86	0.54
P- 85- 500	1957	1.11	0.96	0.96	0.59
P- 85- 550	1934	1.10	1.04	1.04	0.64

Table 1 shows the values of the textural parameters for the three series of ACs. These values were obtained from the adsorption isotherms of N₂ at -196 °C and the curves of the accumulated pore volume versus the pore radius (mercury porosimetry). The highest values of surface area and pore volume correspond to the samples of ACs prepared using phosphoric acid solutions with the higher concentrations (60 or 85%) and heating to the two highest temperatures (500 or 550 °C).

The development of porosity, that results from the carbonisation of the starting material above a certain temperature (>450 °C) through activation with H₃PO₄, is related to the fact that the phosphorus species present in the impregnated product tend to pass into the gas phase, this causing a structural expansion in the product [18]. According to Jaytoyen and Derbyshire [19], the development of porosity below 450 °C is related to the stabilization and expansion of lignocellulosic material structure. Cross-linking reactions begin to dominate over bonds rupture and depolymerisation reactions. These researchers proposed that the formation and stability of the phosphocarbonaceous esters at this temperature limit depolymerisation and consequently the development of porosity.

3.2. Chemical characterization

Regarding the analysis of surface functional groups, the FT-IR spectra obtained for P-60-T series samples showed three very wide bands with maximum absorption peaks located at 3400, 1600 and 1200 cm⁻¹.

At 3400 cm⁻¹ the band associated with O-H stretching vibrations in alcohols and

162 carboxylic acids is located. It should be noted that the intensity of this band in the
163 samples is proportional to the concentration of acid groups found for each of them.
164 The energy absorption in these areas of the infrared spectrum is attributable to the
165 tension vibrations of the O-H, C=C and =CH bonds. The band at 1600 cm^{-1} is due to
166 the presence of C=C groups corresponding to aromatic rings. In the spectrum region
167 around 1200 cm^{-1} , a vibration band is observed in the plane =CH of the aromatics =CH
168 [20]. On the other hand, due to the tension vibration of the P-O and P=O bonds,
169 spectral bands were registered at $1260\text{--}855\text{ cm}^{-1}$ and $1300\text{--}960\text{ cm}^{-1}$, respectively. For
170 P-C bond, however, the band was located between $800\text{--}900\text{ cm}^{-1}$ [21]. Finally, the
171 peak at 1710 cm^{-1} was easily visible in the spectra of these series (see Figure 3).

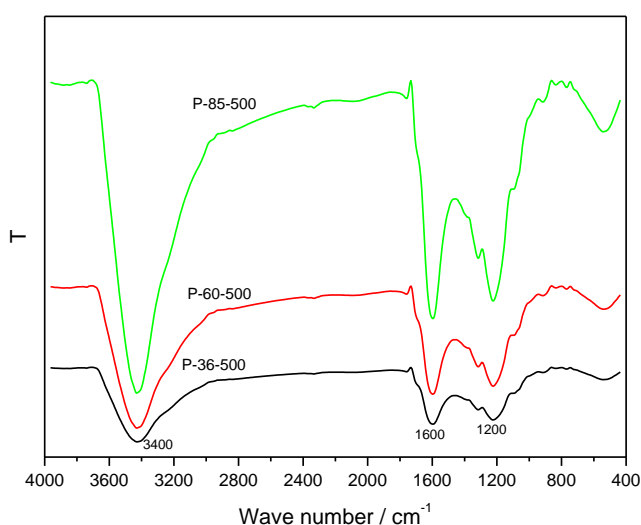


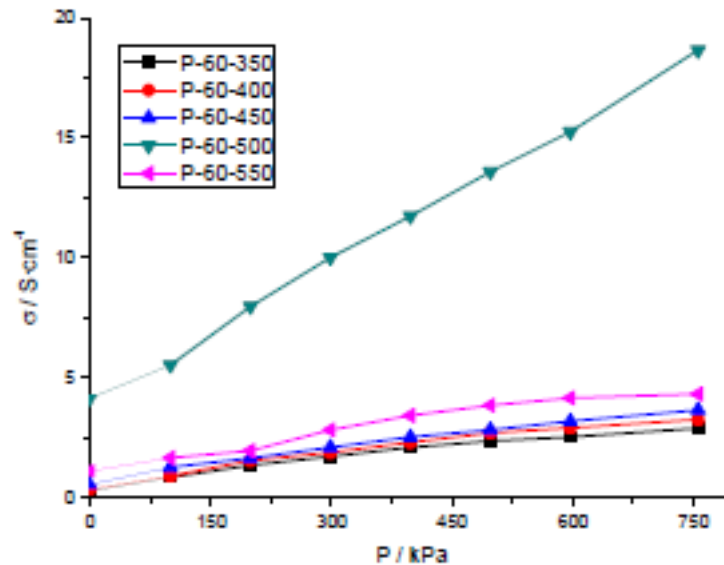
Figure 3. FT-IR spectra for P-T-500 series

3.3. Electrical conductivity

In recent years the application of carbons as electrodes [22-23] has grown due to their electrical conductivity, specific surface, pore distribution, surface chemical composition and easy processibility.

In view of the results obtained, carbons with the largest specific surface area and

180 porosity distribution, series P-60-T, were the object of study in terms of electrical
 181 conductivity. According to the bibliography consulted, this type of carbon can be
 182 good precursors for being used as supercapacitors [10],[24],[25],[26].
 183 Figure 4 shows the variation of the electrical conductivity of the samples (P-60-T
 184 series) with pressure during the compaction process.



185
 186 **Figure 4 Variation of the electrical conductivity with pressure (P-60-T series).**

187 Figure 4 shows that, during the activation process of the carbon, aromatic structures can
 188 be formed, which may favour an increase in conductivity. The increased electrical
 189 conductivity of the P-60-500 sample may be due to the existence of graphical structures,
 190 aromatic rings, oxygen groups, etc., which allows a higher level of mobility to be
 191 produced in the electrons or, in other words: a much higher degree of electricity transfer
 192 is produced.

193 Activated carbon is a carbonaceous material that has a crystalline structure similar to
 194 that of graphite except that the order in the structure of activated carbon is less perfect.
 195 That is to say, the difference between activated carbon and graphite consists in the
 196 degree of arrangement in the three coordinates of the space presented by graphite,
 197 whereas in the CA there are only two, which correspond to the independent planes
 198 constituted by the plates that they conform it, these plates have different orientations.

199 Chemical activation does not produce the same graphite plates that result from the
200 physical activation method. The walls of the carbon rather resemble an organic
201 molecule, part aromatic and part aliphatic, or a polymer highly branched and
202 interlinked, furthermore these walls contain large quantities of atoms other than carbon,
203 mainly oxygen. This fact is verified in the FT-IR spectra where the presence of aromatic
204 structures is evident.

205 Among other reasons, this behaviour may be due to the fact that this carbon forms
206 layers of carbon rings linked together. These rings contain single and double bonds, this
207 giving rise to delocalized electrons by the double bonds of each carbon (pi bonds).
208 These delocalized electrons move from one side to another generating a current when a
209 potential is applied. This phenomenon only takes place if the potential difference goes
210 parallel to the carbon layer. This process does not occur in carbon structures where each
211 carbon is linked to four more carbon through very resistant simple bonds with a null
212 electron delocalization, this being the reason by which they are “tied” to that bond.

213 The behaviour of P-60-550 sample could be due to pulverized activated carbon, which
214 can lead to repulsion problems between its particles and/or decreases in electrical
215 conductivity, as described by various authors in carbon blacks [6].

216 It was observed that when increasing the pressure, the conductivity increased in all
217 samples (see Figure 4). This behaviour is probably due to the loss of porosity and the
218 greater number of contacts between AC particles.

219 If we look at the values obtained for the P-60-T series samples, we can affirm that P-
220 60-450, P-60-500, and P-60-550 samples would be the most suitable to be tested as
221 possible supercapacitors.

222

223 **3.4. Adsorption and electroadsorption of samples prepared by chemical activation**

224 **with H_3PO_4 .**

225 Adsorption consists of the migration of some substances from the gaseous or liquid
226 phase to the surface of a solid substrate. Electroadsorption is generally defined as an
227 adsorption phenomenon induced by a potential difference on the surface of an
228 electrode [27].

229 In these adsorption/electroadsorption processes, the adsorption/electroadsorption
230 velocity will depend fundamentally on the nature of the adsorbent, but also on other
231 factors. In recent years, many researches have been done to understand the behaviour
232 of activated carbon electrodes in electroadsorption processes. It has been shown that
233 the shape, size and pore volume, and pore size distribution have a great influence on
234 the kinetics of electroadsorption [28], [29]. On the other hand, the presence of
235 heteroatoms (such as nitrogen atoms) and/or surface groups in the structure of the
236 activated carbon electrodes can also have a great influence on the electroadsorption
237 processes [28].

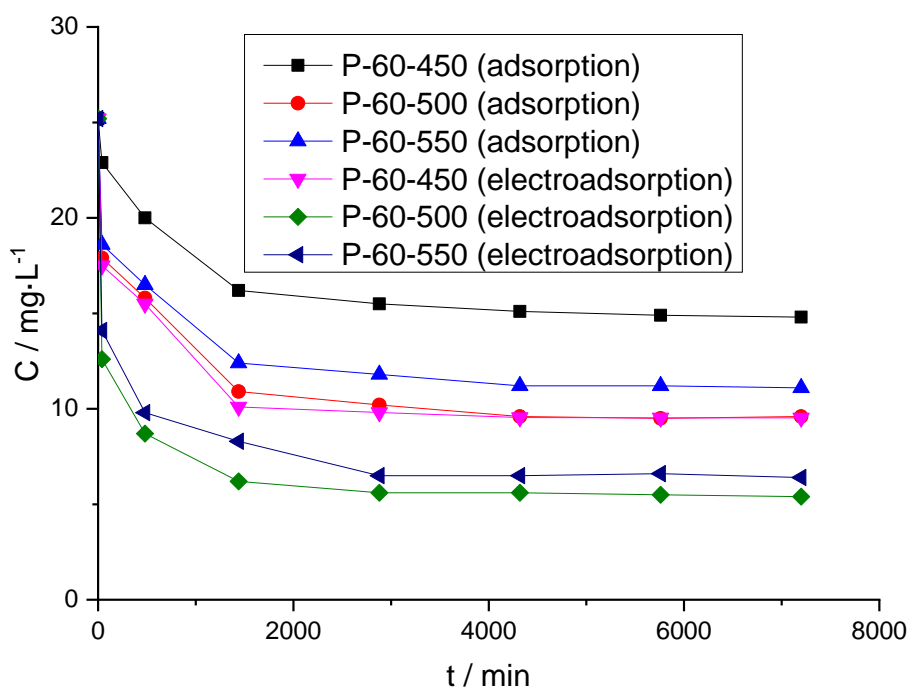
238 In the following section, the results obtained in the kinetics of the adsorption and
239 electroadsorption process are discussed.

240 **3.4.1 Kinetic study**

241 The kinetic study allows determining the rate of adsorbate adsorption and provides an
242 idea of the adsorption mechanism. According to Adamson [30], the step that leads to
243 the link between adsorbate and adsorbent is very fast when taking place a physical
244 adsorption, where the adsorption rate is controlled by the previous diffusion. If
245 adsorption is accompanied by a chemical reaction, adsorption is slow because the
246 chemical reaction is slower than the diffusion step.

247 Kinetic adsorption/electroadsorption models are important in studies carried out on the

248 retention of heavy metal ions in wastewater. In this work, various kinetic models
 249 above described were tested. The velocity constants of each kinetic equation and the
 250 adsorption/electroadsorption parameters were calculated.
 251 The concentration/time kinetic curves are shown in Fig. 5. According to Figure 5, a
 252 rapid adsorption/electroadsorption took place within the first few minutes. After this
 253 initial times the adsorption/electroadsorption gradually decreased, the equilibrium
 254 being reached at different contact times depending on the carbonaceous sample.



255 **Figure 5. Adsorption and electroadsorption kinetics of the prepared samples.**

257 By comparing the kinetics curves of adsorption and electroadsorption, it is observed
 258 that the adsorption process takes place fundamentally in the first 4320 minutes, while
 259 the electroadsorption process is produced within the first 2880 minutes. Subsequently,
 260 it does not significantly increase the amount adsorbed, the equilibrium being reached.

Table 2. Equilibrium times and retained quantities of Cu (II) ions in the kinetic process of adsorption and electroadsorption. Samples activated with H₃PO₄.

Samples	t _e (adsorption) min	q _e mg·g ⁻¹	t _e (electroadsorption) min	q _e mg·g ⁻¹
P-60-450	5760	8.3	4320	12.5
P-60-500	4320	1.5	2880	15.8
P-60-550	4320	1.3	2880	15.0

Likewise, when comparing both processes it is observed that the adsorption equilibrium times are generally greater than those corresponding to electroadsorption (see Table 2). This significant difference in equilibrium times can be explained taking into account that adsorption involves the transfer of a substance from the dissolution to the adsorbent surface. However in electroadsorption, the adsorption process must be supplemented by the action of an external electric field between two electrodes immersed in an electrolytic solution. This electric field causes the charged ions to be forced to move towards the opposing charge electrodes, this giving rise to a charge separation throughout the electrode/dissolution interface [15-16].

Both in adsorption and electroadsorption process, the same sequence of adsorption capacity of the samples was observed, this being P-60-500 > P-60-550 > P-60-450. This fact could be related, on the one hand, to the presence of superficial groups, and, on the other hand, to the distribution of porosity in the samples. In particular, it could be related to the mesopores, which would facilitate the diffusion of adsorbate into the activated carbon, as observed in sample P-60-500 and gathered in Table 1 ($V_{me, narrow} = 1.15 \text{ cm}^3 \cdot \text{g}^{-1}$, and $V_{me, wide} = 0.35 \text{ cm}^3 \cdot \text{g}^{-1}$).

3.4.1.1. Kinetic models of the processes

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288 The design and study of an adsorption system requires knowledge of the equilibrium
289 and kinetics of adsorption. The kinetics of a chemical process depends on material
290 factors (adsorbents and adsorbates used) such as experimental factors (temperature and
291 pH) [31-32]. The two most used kinetic models in the study of the adsorption process
292 in liquids are pseudo-first-order and pseudo-second-order . Numerous studies have
293 attempted to rationalize these two empirical models [33-36] and review their
294 applications to different chemical systems [37-39].

295 On the other hand, the theoretical complexity of adsorption mechanisms has developed
296 different kinetic models to predict the amount of adsorbate adsorbed on the adsorbent
297 [37], [40-41].

298 Considering the complexities and restriction of the theoretical models, the empirical or
299 at best 'rationalized' empirical models, such as the pseudo- order models, shall remain
300 relevant and attractive in the modelling of liquid adsorption kinetics for practical
301 purposes.

302 *3.4.1.1.1 Pseudo-first order model*

303 The pseudo-first order kinetics are based on the hypothesis that each metallic ion is
304 assigned an adsorption site of the adsorbent material.

305 To check whether the adsorption/electroabsorption process of copper ions on activated
306 carbon complies with the mathematical expression applicable to the first order
307 kinetics, a linear adjustment of the experimental data was performed.

308 Graphs of $\log(q_e - q_t)$ versus time of the adsorption process are shown in Figure 6. The
309 values of k_1 and the correlation coefficient, R^2 , for all samples are gathered in Table 3.
310 R^2 values varied from 0.9028 to 0.9684 for the adsorption process (see Table 3-A), and
311 from 0.7219 to 0.9521 for the electroadsorption process (see Table 3-B). Likewise, a
312 bad correlation was observed between the values of experimental q_e (see Table 2) and

313 those obtained by the pseudo-first order model (see Table 3)

314 Therefore, we can conclude that neither of the two processes fits well with the pseudo-
315 first order model. However, the Cu (II) ion adsorption fits better than its
316 electroadsorption.

317 **Table 3. Kinetic parameters of adsorption (A) and electroadsorption (B).**

318 (A) Adsorption

Samples	Pseudo-primer order			Pseudo-second order		
	q _e	k ₁	R	q _e	k ₂	R
P-60-450	5.9	7.7·10 ⁻⁴	0.9684	8.7	3.5·10 ⁻⁴	0.9981
P-60-500	8.2	1.1·10 ⁻³	0.9028	1.8	4.3·10 ⁻⁴	0.9986
P-60-550	6.4	8.6·10 ⁻⁴	0.9295	1.6	4.6·10 ⁻⁴	0.9990

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Samples	Diffusion		
	C	k _{id}	R
P-60-450	3.2	1.6·10 ⁻¹	0.9970
P-60-500	2.5	2.3·10 ⁻¹	0.9993
P-60-550	0.9	1.3·10 ⁻¹	0.9958

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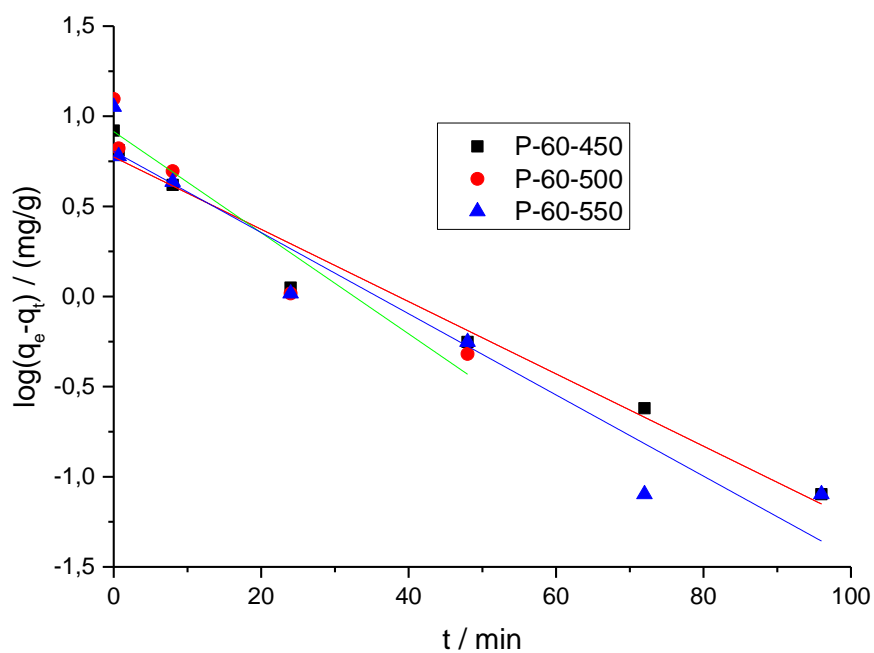
322 (B) Electroadsorption

Samples	Pseudo-primer order			Pseudo-second order		
	q _e	k ₁	R	q _e	k ₂	R
P-60-450	8.8	1.6·10 ⁻³	0.9521	12.8	5.6·10 ⁻⁴	0.9988
P-60-500	5.0	8.4·10 ⁻⁴	0.8205	15.9	1.0·10 ⁻³	0.9999
P-60-550	5.2	8.4·10 ⁻⁴	0.7219	15.2	7.3·10 ⁻⁴	0.9996

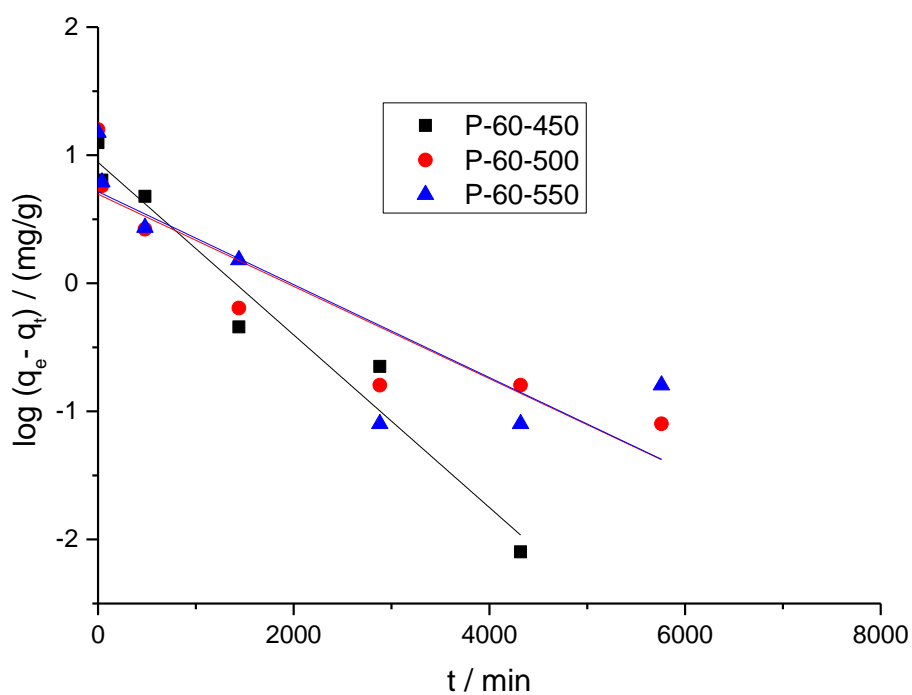
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Samples	Diffusion		
	C	k _{id}	R
P-60-450	4.5	1.9·10 ⁻¹	0.8918
P-60-500	9.6	2.6·10 ⁻¹	0.9507
P-60-550	8.3	1.5·10 ⁻¹	0.9835



(A)



(B)

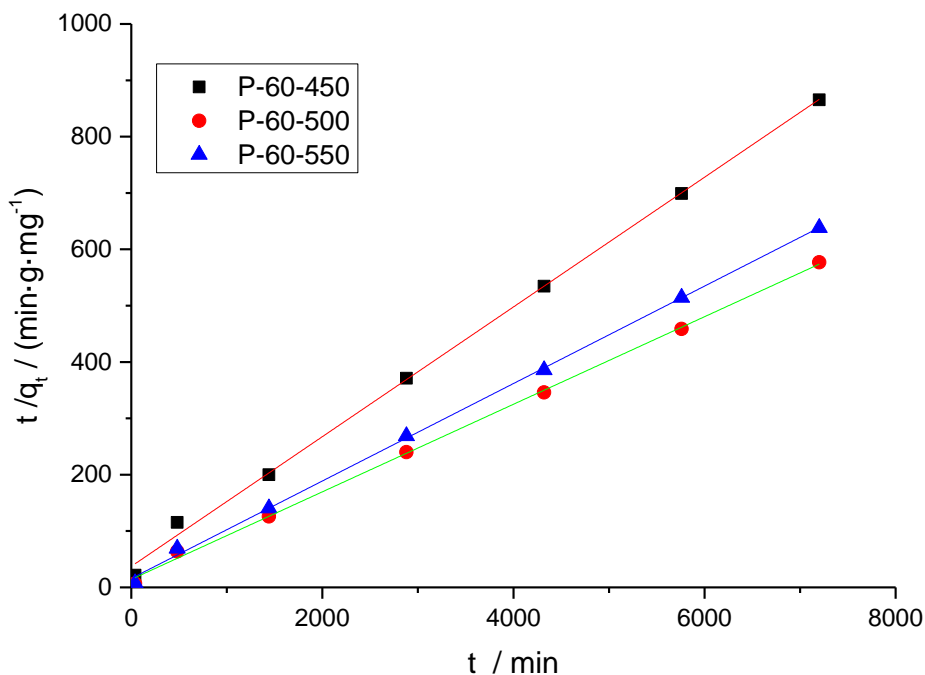
Figure 6. Graphic representation of the pseudo-first order model: (A) adsorption, (B) electroadsorption.

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333 *3.4.1.1.2 Pseudo-second order model*

334 The experimental data were adjusted to the pseudo-second order kinetic model. Figure
335 3.5 shows the graphs that represents t/q_t versus time. From the slope the q_e value was
336 obtained, while the intercept provided the k_2 value.

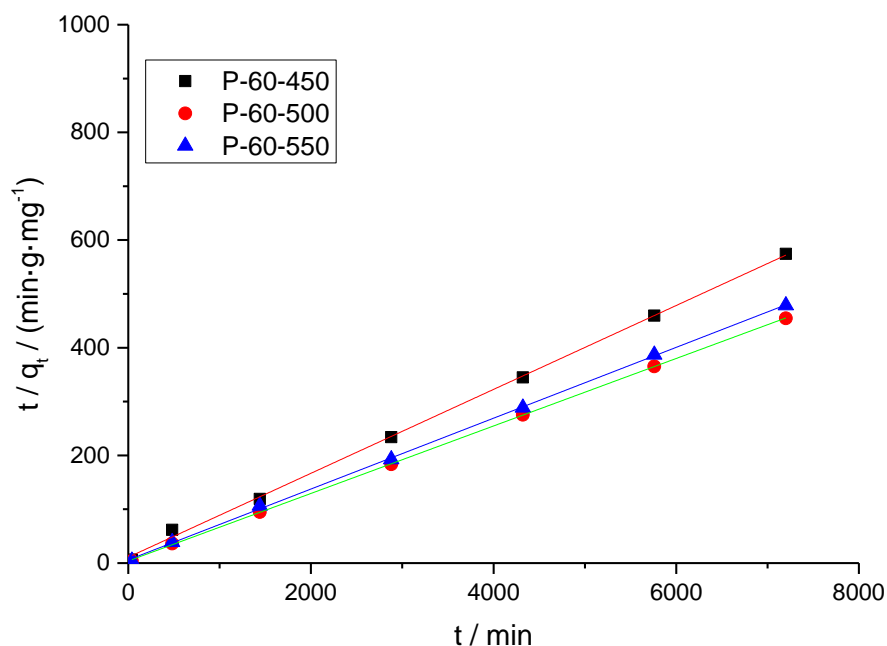
337 The kinetic parameters obtained in the adsorption/electroadsorption process are
338 gathered in Table 3. This model fits better than the pseudo-first order model according
339 to the values of the correlation coefficients R^2 , which are closer to the unit. This
340 indicates that copper is chemisorbed on the surface of the activated carbon. Similar
341 behaviour was reported by other authors for this type of adsorption kinetic model
342 applied to other metals [42-47].



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(A)



(B)

Figure 7. Graphic representation of pseudo-second order model: (A) adsorption; (B) electroadsorption

Figure 7 shows how the kinetic model of pseudo-second order suitably describes the adsorption of copper in the activated carbon samples prepared in this series. Moreover, and as gathered in Table 3, the correlation coefficients were generally higher than 0.9981 and were over the obtained with the pseudo-first order model. This suitable behaviour could be explained by the adsorption/electroadsorption mechanism in the process, which involves the valence forces through the sharing or exchange of electrons between the copper ions and the adsorbent. In addition, the adsorption capacity of activated carbons is directly proportional to the active sites occupied by copper ions, which means that adsorbate is adsorbed in two active sites of activated carbons.

Table 3 shows that the values of R^2 are closer to 1 in electroadsorption kinetics than in adsorption kinetics. Therefore, it can be affirmed that the pseudo-second order model

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361 is better adjusted to the electroadsorption process of the samples under study.

362 In the particular case of adsorption, and as gathered in Table 3, it was observed that
363 the P-60-450 sample had lower kinetic parameters than the P-60-500 and P-60-550
364 samples. This indicates, on the one hand, that kinetics are slower (k_2 lower), and, on
365 the other hand, that the concentration in the equilibrium q_e ($8.3 \text{ mg}\cdot\text{g}^{-1}$) is similar to
366 the q_e calculated by the kinetic model ($8.7 \text{ mg}\cdot\text{g}^{-1}$). Kinetic behaviour is similar for the
367 samples P-60-500 and P-60-550, as reflected in the kinetic parameters gathered in
368 Table 3.3. This could be related to the similar porous texture (see Table 1) and the
369 presence of oxygenated groups in both samples (see Figure 3).

370 On the other hand, in the electroadsorption process (see Table 3.B), it is observed that
371 the k_2 value of the P-60-500 sample is greater than those corresponding to the other
372 samples, which indicates that its kinetics is faster. This faster kinetic could be related
373 not only to the presence of superficial groups, but also to the presence of mesoporous
374 structures previously mentioned. Also, the correlation between the experimental q_e
375 values (see Table 2) and the calculated q_e values (see Table 3) through the pseudo-
376 second order kinetic model was very good.

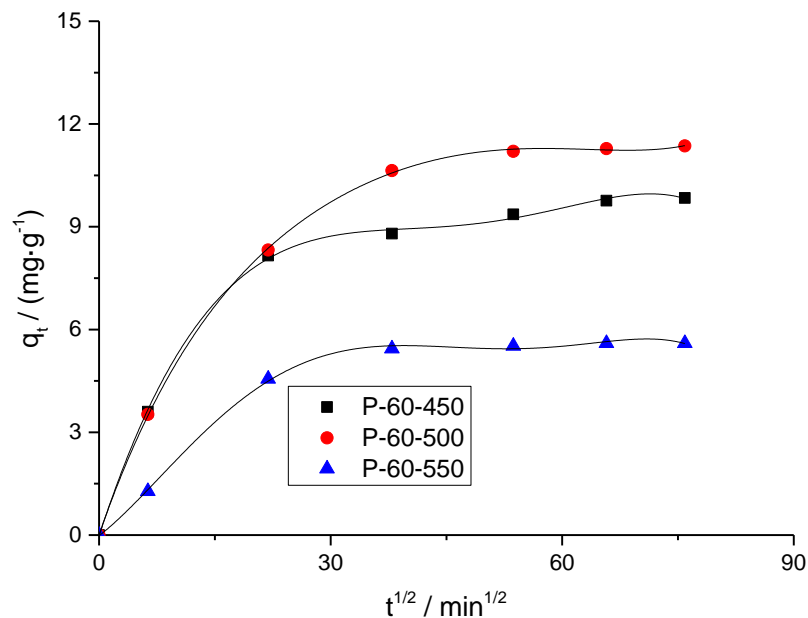
377 According to the obtained results, it can be concluded that both processes are well
378 adjusted to the kinetic model of pseudo-second order, especially for electroadsorption
379 process.

380 *3.4.1.1.3. Intraparticle diffusion*

381 The Weber and Morris intraparticle diffusion model was also used to describe the
382 kinetics of Cu (II) absorption. This model assumes that if the regression of q_t vs. $t^{1/2}$ is
383 linear and passes through the origin, intraparticle diffusion is the only rate-limiting
384 step[48-50]. However, this is not always the case, since other processes, such as surface
385 diffusion and equilibrium adsorption, may also limit the velocity at different stages of

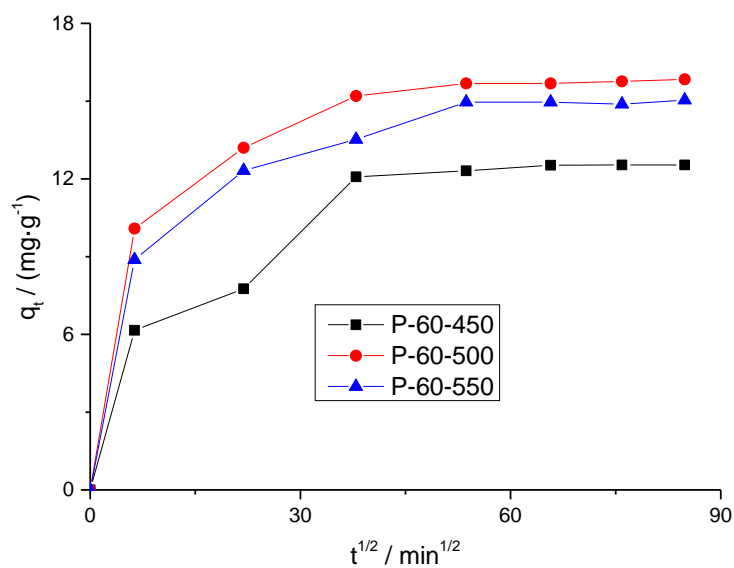
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386 the kinetic profile, which would result in a multi-linearity in the intraparticle diffusion
387 plot [51].
388 Plots of q_t versus $t^{1/2}$ for the adsorption (see Figure 8-A) and electroadsorption process
389 (see Figure 8-B) show two linear sections. The slope of the first section, approximately
390 between 6 and 40 $\text{min}^{1/2}$, corresponds to the two adsorption/electroadsorption processes
391 and is more pronounced than the slope of the second section. This difference shows that
392 the diffusion process is faster in this first section. This fact would be associated with the
393 diffusion of adsorbate through the liquid-solid interface, the linear behaviour indicating
394 a quickly mass transport. The second linear section corresponds to values of $t^{1/2}$ between
395 53 and 87 $\text{min}^{1/2}$ and is associated with the transport of adsorbate into the adsorbent
396 pores (internal diffusion). This behaviour seems to also indicate that this stage takes
397 place quickly. However, from samples shown in Figure 8, it is deduced that the values
398 of the correlation coefficients are quite different from the unit (see Table 3).



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(A)



(B)

Figure 8. Graphic representation of the intraparticle diffusion model: (A) adsorption; (B) electroadsorption.

In general, it is observed that mass diffusion values, from the surface to the interior of activated carbon (k_{dif}), and the boundary of the mass transfer layer (C) are increased in the electroadsorption process (see Table 3). Higher values of C indicate a greater surface participation in metal adsorption. For P-60-500 and P-60-550 samples, which have the best electroadsorption capacity, the highest values of q_t can be observed, while P-60-500 sample has the best adsorption capacity.

4. Conclusions

The preparation, characterization and use of activated carbons was carried out in this study. Prepared samples showed a high specific surface area and notable porous development.

The increase of the concentration of the solution of phosphoric acid, activant agent, develops in the samples a greater superficial area and an increase in the volume of micropore; furthermore it has an influence on the superficial chemistry of the

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419 carbonaceous material, presenting variations in the quantity of acid groups, which were
420 characterized by infrared spectroscopy.

421 From textural parameters, chemical analysis and electrical conductivity, the three best
422 activated carbons were selected for their application in the adsorption/electroadsorption
423 process, these being P-60-450, P-60-500, and P-60-550.

424 The equilibrium time in the electroadsorption process was lower than the equilibrium
425 time in the adsorption process. The pseudo-second order model fitted better than the
426 pseudo-first order model, since the values of the correlation coefficients R^2 were closer
427 to the unit. This indicates that copper is chemisorbed on the surface of the activated
428 carbon.

429 [Intraparticle diffusion plots have two stages. The first stage is due to an instantaneous](#)
430 [adsorption or adsorption on the outer surface, where the adsorbate travels to the outer](#)
431 [surface of the adsorbent. In the second stage a gradual adsorption occurs where the](#)
432 [intraparticle diffusion is the velocity limiting, i.e., the adsorbate travels within the pores](#)
433 [of the adsorbent.](#)

434 Thus, according to the results obtained, the sample with the highest copper retention
435 capacity was sample P-60-500. The greater elimination capacity of the Cu (II) ions
436 evidenced by the sample P-60-500, due to its harmful effects on health and the
437 environment, is undoubtedly a result of great interest.

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439 **5. References**

- 440 [1] C. Santhosh, V. Velmurugan, G. Jacob, S. K. Jeong, A. N. Grace, and A.
441 Bhatnagar, "Role of nanomaterials in water treatment applications: A review,"
442 *Chem. Eng. J.*, vol. 306, pp. 1116–1137, 2016.
- 443 [2] G. A. Adebisi, Z. Z. Chowdhury, and P. A. Alaba, "Equilibrium, kinetic, and
444 thermodynamic studies of lead ion and zinc ion adsorption from aqueous solution
445 onto activated carbon prepared from palm oil mill effluent," *J. Clean. Prod.*, vol.

- 446 148, pp. 958–968, 2017.
- 1
2 447 [3] N. P. Raval, P. U. Shah, and N. K. Shah, “Adsorptive removal of nickel(II) ions
3 448 from aqueous environment: A review,” *J. Environ. Manage.*, vol. 179, pp. 1–20,
4 449 2016.
- 5
6
7 450 [4] M. Ramesh, “Kenaf (*Hibiscus cannabinus* L.) fibre based bio-materials: A review
8 on processing and properties,” *Prog. Mater. Sci.*, vol. 78–79, pp. 1–92, 2016.
- 9 451
10 452 [5] M. S. Shamsuddin, N. R. N. Yusoff, and M. A. Sulaiman, “Synthesis and
11 Characterization of Activated Carbon Produced from Kenaf Core Fiber Using
12 453 H₃PO₄ Activation,” *Procedia Chem.*, vol. 19, pp. 558–565, 2016.
- 13 454
14 455 [6] E. M. Cuerda-Correa, A. Macías-García, M. A. D. Díez, and A. L. Ortiz,
15 456 “Textural and morphological study of activated carbon fibers prepared from
16 kenaf,” *Microporous Mesoporous Mater.*, vol. 111, no. 1–3, pp. 523–529, 2008.
- 17 457
18 458 [7] Y. Sun, H. Li, G. Li, B. Gao, Q. Yue, and X. Li, “Characterization and
19 ciprofloxacin adsorption properties of activated carbons prepared from biomass
20 459 wastes by H₃PO₄ activation,” *Bioresour. Technol.*, vol. 217, pp. 239–244, 2016.
- 21 460
22 461 [8] B. Meryemoglu, S. Irmak, and A. Hasanoglu, “Production of activated carbon
23 materials from kenaf biomass to be used as catalyst support in aqueous-phase
24 462 reforming process,” *Fuel Process. Technol.*, vol. 151, pp. 59–63, 2016.
- 25 463
26 464 [9] M. Bilal *et al.*, “Waste biomass adsorbents for copper removal from industrial
27 wastewater-A review,” *J. Hazard. Mater.*, vol. 263, pp. 322–333, 2013.
- 28 465
29 466 [10] D. Kołodyńska, J. Krukowska, and P. Thomas, “Comparison of sorption and
30 desorption studies of heavy metal ions from biochar and commercial active
31 467 carbon,” *Chem. Eng. J.*, vol. 307, pp. 353–363, 2017.
- 32 468
33 469 [11] A. Macías-García, M. Gómez Corzo, M. Alfaro Domínguez, M. Alexandre
34 Franco, and J. Martínez Naharro, “Study of the adsorption and electroadsorption
35 470 process of Cu (II) ions within thermally and chemically modified activated
36 carbon,” *J. Hazard. Mater.*, vol. 328, pp. 46–55, 2017.
- 37 471
38 472 [12] Z. Z. Chowdhury, S. M. Zain, R. A. Khan, and M. S. Islam, “Preparation and
39 characterizations of activated carbon from kenaf fiber for equilibrium adsorption
40 473 studies of copper from wastewater,” *Korean J. Chem. Eng.*, vol. 29, no. 9, pp.
41 474 1187–1195, 2012.
- 42 475
43 476 [13] C. M. Hasfalina, R. Z. Maryam, C. A. Luqman, and M. Rashid, “Adsorption of
44 Copper (II) From Aqueous Medium In Fixed-Bed Column By Kenaf Fibres,”
45 477 *APCBEE Procedia*, vol. 3, no. May, pp. 255–263, 2012.
- 46 478
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- 480 [14] Y. Han, X. Quan, S. Chen, H. Zhao, C. Cui, and Y. Zhao, "Electrochemically
481 enhanced adsorption of phenol on activated carbon fibers in basic aqueous
482 solution," *J. Colloid Interface Sci.*, vol. 299, no. 2, pp. 766–771, 2006.
- 483 [15] H. Li, Y. Gao, L. Pan, Y. Zhang, Y. Chen, and Z. Sun, "Electrosorptive
484 desalination by carbon nanotubes and nanofibres electrodes and ion-exchange
485 membranes," *Water Res.*, vol. 42, no. 20, pp. 4923–4928, 2008.
- 486 [16] E. J. Bain, J. M. Calo, R. Spitz-steinberg, J. Kirchner, and J. Ax, "Electrosorption
487 / Electrodesorption of Arsenic on a Granular Activated Carbon in the Presence of
488 Other Heavy Metals †," *Energy Fuels*, pp. 3415–3421, 2010.
- 489 [17] M. E. Ramos, P. R. Bonelli, and A. L. Cukierman, "Physico-chemical and
490 electrical properties of activated carbon cloths. Effect of inherent nature of the
491 fabric precursor," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 324, no. 1–3,
492 pp. 86–92, 2008.
- 493 [18] M. Olivares-Marín, C. Fernández-González, A. Macías-García, and V. Gómez-
494 Serrano, "Porous structure of activated carbon prepared from cherry stones by
495 chemical activation with phosphoric acid," *Energy and Fuels*, vol. 21, no. 5, pp.
496 2942–2949, 2007.
- 497 [19] M. Jagtoyen and F. Derbyshire, "Activated carbons from yellow poplar and white
498 oak by H3PO4 activation," *Carbon N. Y.*, vol. 36, no. 7–8, pp. 1085–1097, 1998.
- 499 [20] J. Karen, H. Peña, Liliana Giraldo, Juan Carlos Moreno. Preparation of activated
500 carbon from orange peel by chemical activation. Physical and chemical
501 characterization. *Rev. Colomb. Quím.*, 41(2): 311-323, 2012
- 502 [21] [W. Pretsch, E. Clerc, T. Seibl, J. Simon, "Tables of Spectral Data for Structure
503 Determination of Organic Compounds". Translation by K. Biemann.
504 Springer- Verlag, Berlin, Heidelberg, New York, Tokyo, 1983. 316 pp.](#)
- 505 [22] E. Frackowiak and F. Beguin, "Carbon Materials for the Electrochemical Storage
506 of Energy in capacitors," *Carbon N. Y.*, vol. 39, pp. 937–950, 2001.
- 507 [23] D. Qu, D. Qu, H. Shi, and H. Shi, "Studies of activated carbons used in double-
508 layer capacitors," *Construction*, pp. 99–107, 1998.
- 509 [24] A. G. Pandolfo and A. F. Hollenkamp, "Carbon properties and their role in
510 supercapacitor.pdf," *J. Power Sources*, vol. 157, no. 1, pp. 11–27, 2006.
- 511 [25] [A. B. Fuertes, F. Pico, and J. M. Rojo, "Influence of pore structure on electric
512 double-layer capacitance of template mesoporous carbons," *J. Power Sources* ,
513 vol. 133, no 2, pp. 329–336, 2004.](#)

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49
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52
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56
57
58
59
60
61
62
63
64
65
- 514 [26] E. Frackowiak and F. Béguin, “Carbon materials for the electrochemical storage
515 of energy in capacitors,” *Carbon N. Y.*, vol. 39, no. 6, pp. 937–950, 2001.
516
- 517 [27] S. Lagergren, “About the theory of so-called adsorption of soluble substance,”
518 *Kungliga Svenska Vetenskap akademien Handlingar*, vol. 24, pp. 1–39, 1898.
- 519 [28] B. E. Conway, *Electrochemical Supercapacitors-Scientific Fundamentals and*
520 *Technological Applications. Publishing: New York, N.Y.: Kluwer Academic /*
521 *Plenum Publishers, 1999.*
- 522 [29] Y. R. Nian and H. Teng, “Influence of surface oxides on the impedance behavior
523 of carbon-based electrochemical capacitors,” *J. Electroanal. Chem.*, vol. 540, pp.
524 119–127, 2003.
- 525 [30] M. A. Adamson, *Physical and Chemistry of Surface*. Publishing: John Wiley &
526 Sons Inc,1980.
- 527 [31] R. Slimani , A. Anouzla, Y. Abrouki, et al. Removal of a cationic dye -Methylene
528 Blue- from aqueous media by the use of animal bone meal as a new low cost
529 adsorbent. *J Mater Environ Sci.* 2:77–87, 2011 .
530
- 531 [32] A. Regti, M.R. Laamari, S-E.Stiriba, M. El Haddad. Use of response factorial de-
532 sign for process optimization of basic dye adsorption onto activated carbon
533 derived from Persea species. *Microchem J*, 130:129–36, 2017 .
- 534 [33] Y. Liu Y , Z-W.Wang. Uncertainty of preset-order kinetic equations in
535 description of biosorption data. *Bioresour Technol* 99:3309–12, 2008 .
- 536 [34] A. Özer. Removal of Pb(II) ions from aqueous solutions by sulphuric acid-treated
537 wheat bran. *J Hazard Mater* 141:753–61, 2007 .
- 538 [35] C-I.Lin, L-H.Wang. Rate equations and isotherms for two adsorption models. *J*
539 *Chin Inst Chem Eng* 39:579–85, 2008 .
- 540 [36] Y. Liu, S-F Yang, H. Xu , K-H Woon, Y-M Lin, J-H Tay . Biosorption kinetics
541 of cadmium(II) on aerobic granular sludge. *Process Biochem* 38:997–10 01,
542 2003.
- 543 [37] G. Alberti, V. Amendola, M. Pesavento, R. Biesuz . Beyondthesynthesis of novel
544 solid phases: review on modelling of sorption phenomena. *Coord Chem Rev*
545 256:28–45, 2012 .
- 546 [38] YS Ho. Review of second-order models for adsorption systems. *J Hazard Mater*
547 136:681–9, 2006 .

- 548 [39] Y. Liu Y , YJ Liu. Biosorption isotherms, kinetics and thermodynamics. *Sep Purif*
549 *Technol* 61:229–42, 2008 .
- 550 [40] W. Plazinski, W. Rudzinski, A. Plazinska. Theoretical models of sorption
551 kinetics including a surface reaction mechanism: a review. *Adv Colloid Interface*
552 *Sci* 152:2–13, 2009.
- 553 [41] K.L. Tan, B.H. Hameed. Insight into the adsorption kinetics models for the
554 removal of contaminants from aqueous solutions. *Journal of the Taiwan Institute of*
555 *Chemical Engineers* 74 25–48, 2017.
- 556 [42] M. Madhava Rao, A. Ramesh, G. Purna Chandra Rao, and K. Sessaiah,
557 “Removal of copper and cadmium from the aqueous solutions by activated
558 carbon derived from Ceiba pentandra hulls,” *J. Hazard. Mater.*, vol. 129, no. 1–3,
559 pp. 123–129, 2006.
- 560 [43] M. M. Rao, D. K. Ramana, K. Sessaiah, M. C. Wang, and S. W. C. Chien,
561 “Removal of some metal ions by activated carbon prepared from Phaseolus
562 aureus hulls,” *J. Hazard. Mater.*, vol. 166, no. 2–3, pp. 1006–1013, 2009.
- 563 [44] V. C. Srivastava, I. D. Mall, and I. M. Mishra, “Adsorption of toxic metal ions
564 onto activated carbon. Study of sorption behaviour through characterization and
565 kinetics,” *Chem. Eng. Process. Process Intensif.*, vol. 47, no. 8, pp. 1275–1286,
566 2008.
- 567 [45] J. Acharya, J. N. Sahu, C. R. Mohanty, and B. C. Meikap, “Removal of lead(II)
568 from wastewater by activated carbon developed from Tamarind wood by zinc
569 chloride activation,” *Chem. Eng. J.*, vol. 149, no. 1–3, pp. 249–262, 2009.
- 570 [46] J. Anandkumar and B. Mandal, “Removal of Cr(VI) from aqueous solution using
571 Bael fruit (*Aegle marmelos correa*) shell as an adsorbent,” *J. Hazard. Mater.*, vol.
572 168, no. 2–3, pp. 633–640, 2009.
- 573 [47] S. Chen, Q. Yue, B. Gao, Q. Li, and X. Xu, “Removal of Cr(VI) from aqueous
574 solution using modified corn stalks: Characteristic, equilibrium, kinetic and
575 thermodynamic study,” *Chem. Eng. J.*, vol. 168, no. 2, pp. 909–917, 2011.
- 576 [48] E. Asuquo, A. Martin, P. Nzerem, F. Siperstein, and X. Fan, “Adsorption of
577 Cd(II) and Pb(II) ions from aqueous solutions using mesoporous activated carbon
578 adsorbent: Equilibrium, kinetics and characterisation studies,” *J. Environ. Chem.*
579 *Eng.*, vol. 5, no. 1, pp. 679–698, 2017.
- 580 [49] A. Mittal, A. Malviya, D. Kaur, J. Mittal, and L. Kurup, “Studies on the

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581 adsorption kinetics and isotherms for the removal and recovery of Methyl Orange
582 from wastewaters using waste materials,” *J. Hazard. Mater.*, vol. 148, no. 1–2,
583 pp. 229–240, 2007.

584 [50] Y. Huang, S. Li, J. Chen, X. Zhang, and Y. Chen, “Adsorption of Pb(II) on
585 mesoporous activated carbons fabricated from water hyacinth using
586 H3PO4activation: Adsorption capacity, kinetic and isotherm studies,” *Appl. Surf.
587 Sci.*, vol. 293, pp. 160–168, 2014.

588 [51] H. Qiu, L. Lv, B. Pan, Q. Zhang, W. Zhang, and Q. Zhang, “Critical review in
589 adsorption kinetic models,” *J. Zhejiang Univ. A*, vol. 10, no. 5, pp. 716–724,
590 2009.

Figure 1. Adapter designed in 3D to be incorporated into a therm
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Figure 2. System of integrated electrodes (designed in 3D).
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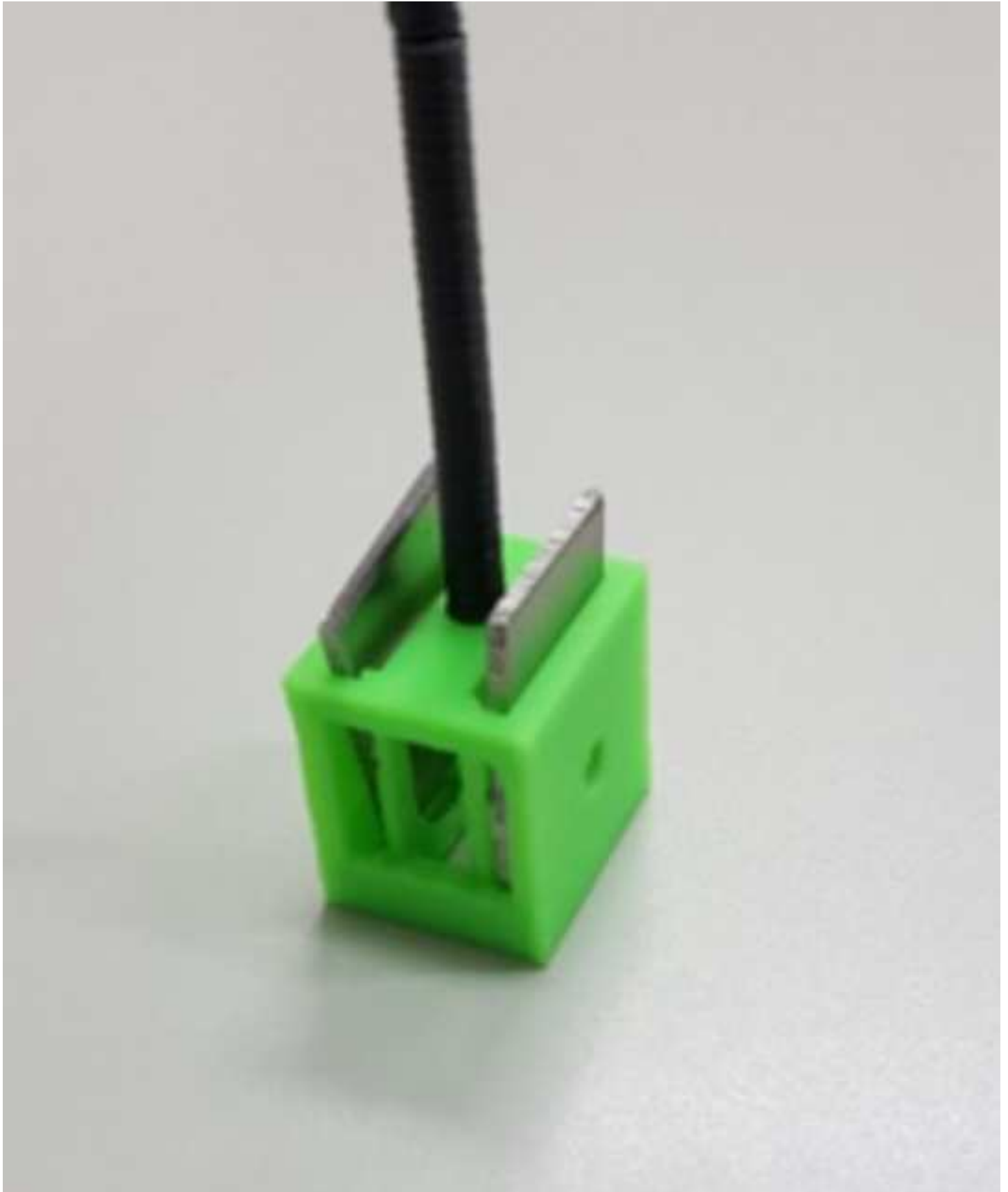


Figure 3. FT-IR spectra for P-T-500 series
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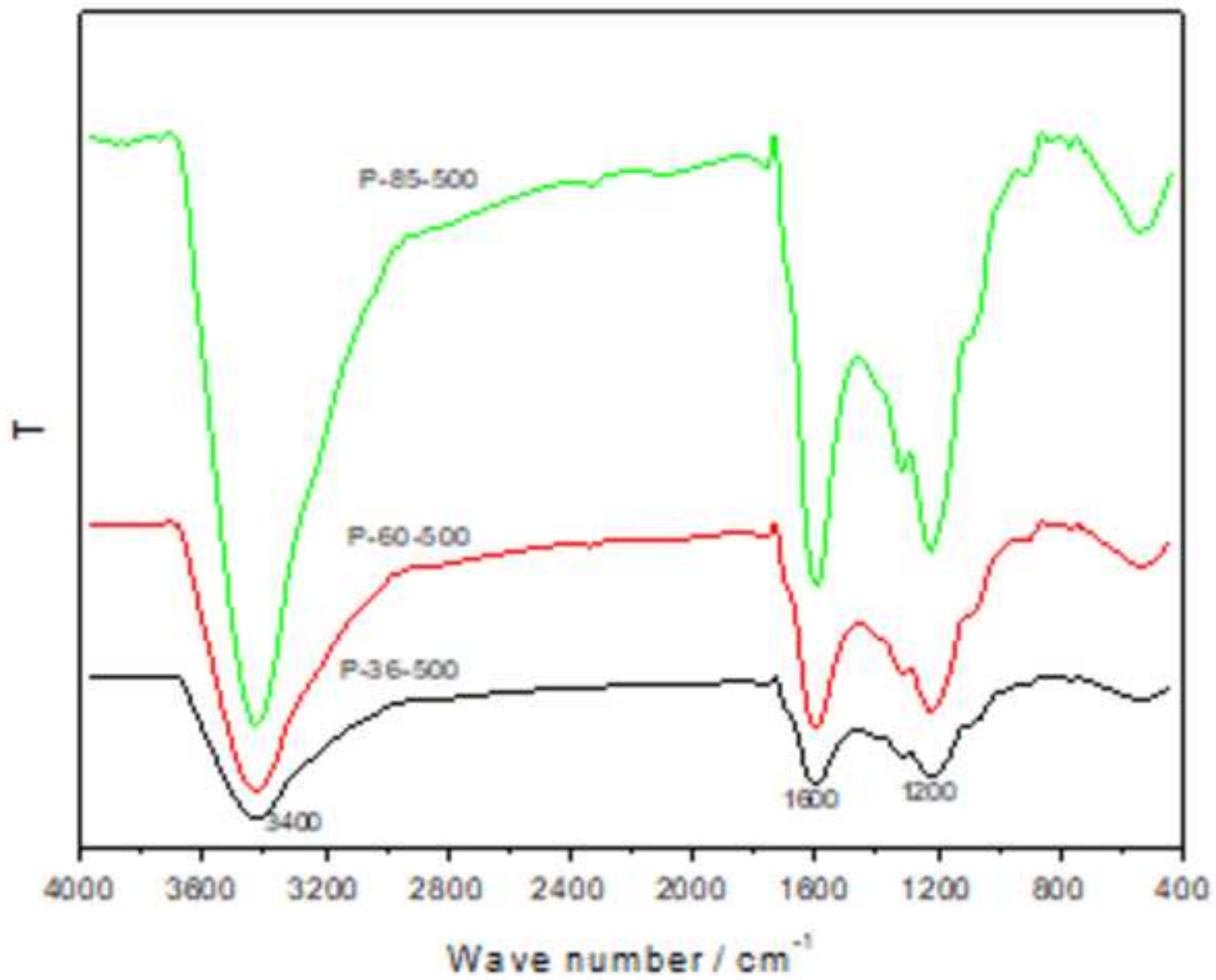


Figure 4 Variation of the electrical conductivity with pressure
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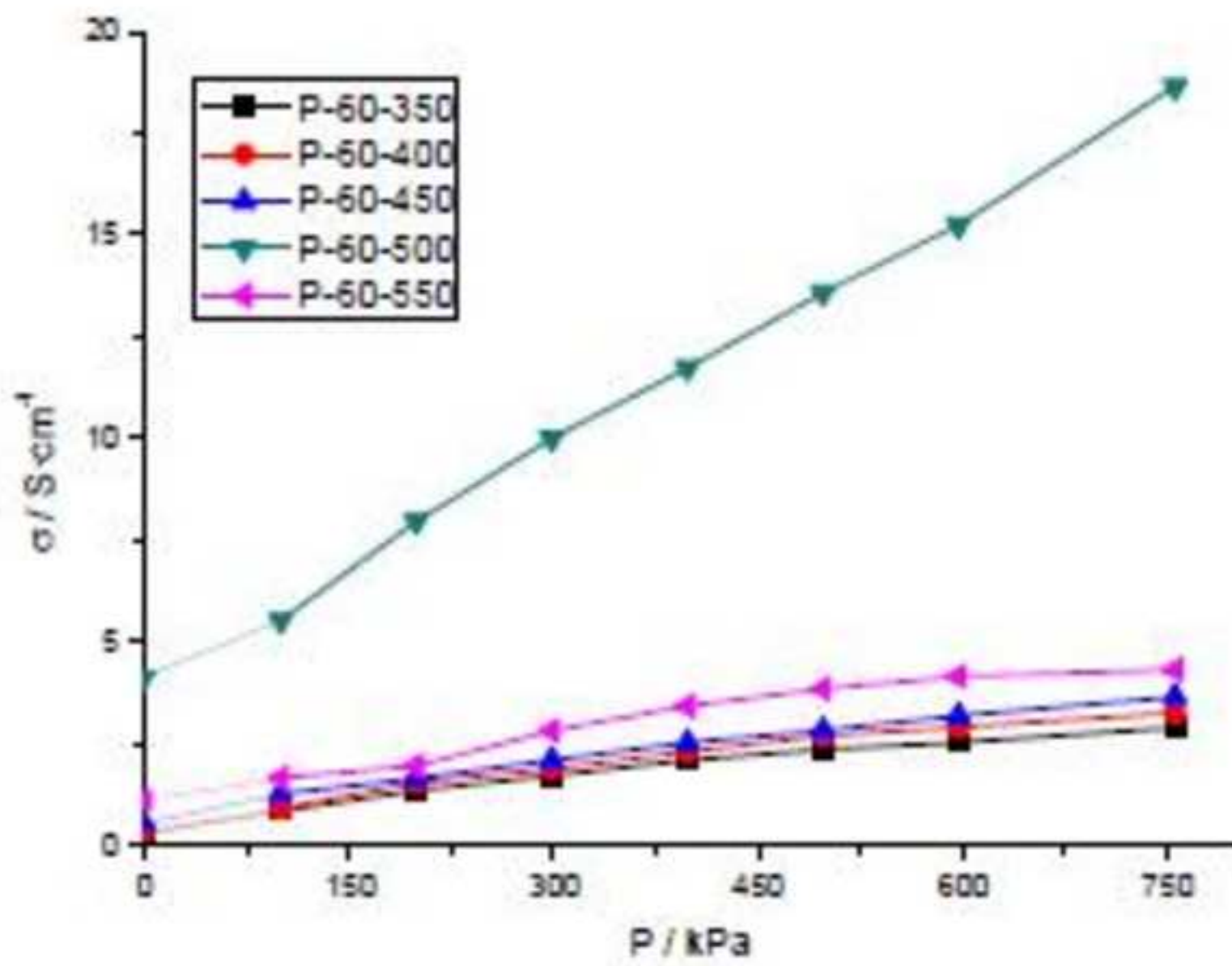


Figure 5. Adsorption and electroadsorption kinetics of the prepa
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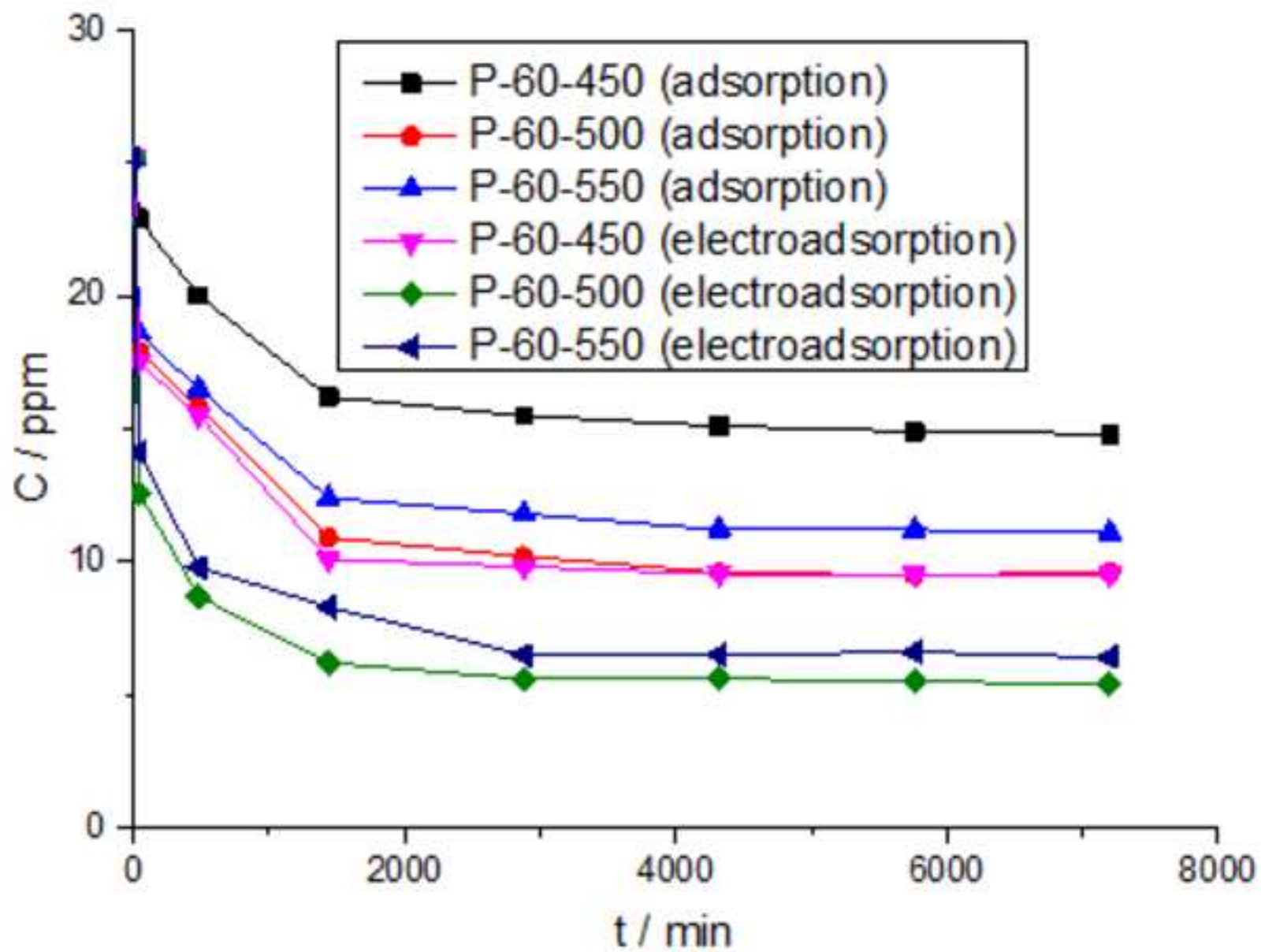
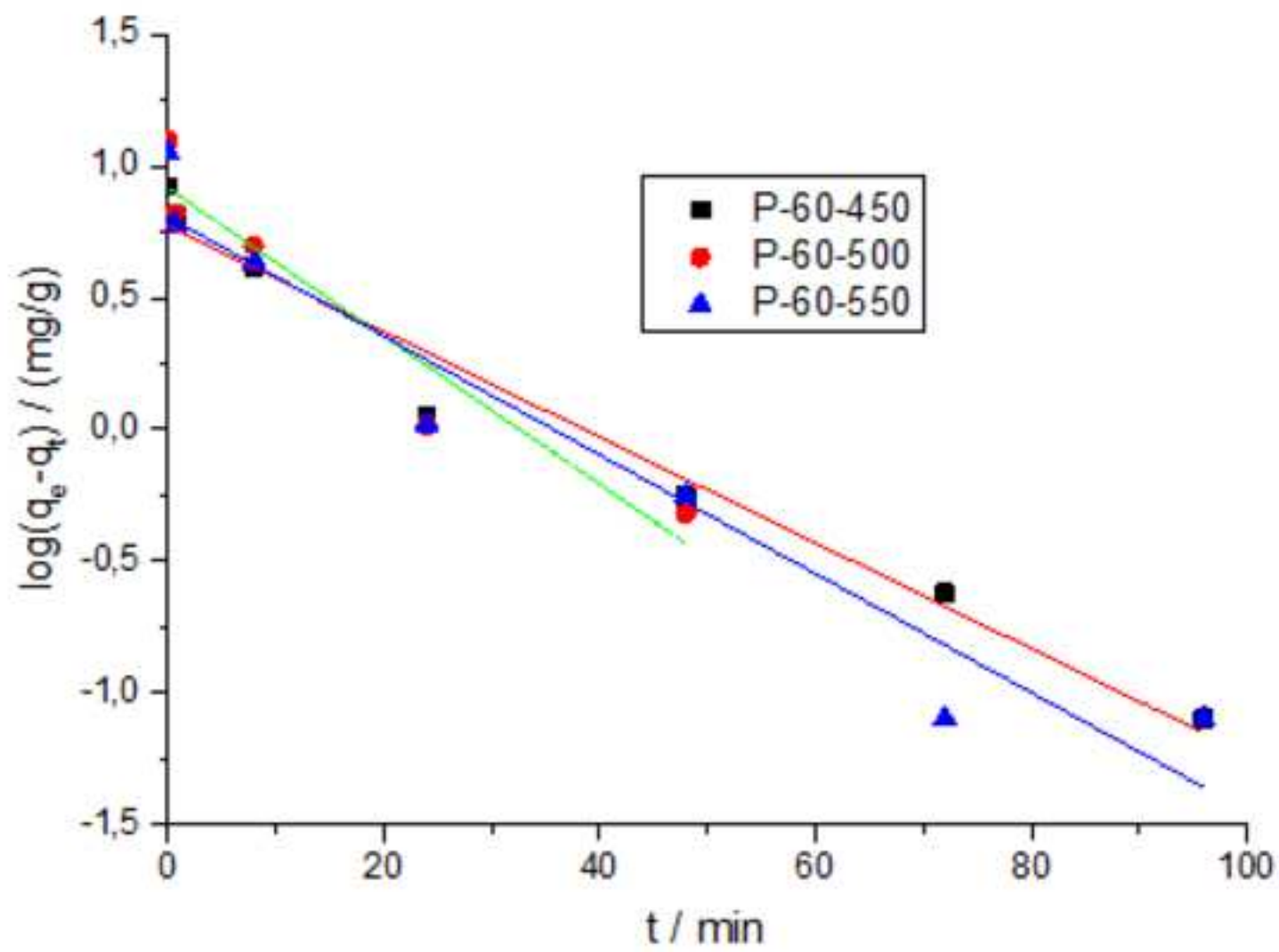


Figure 6. Pseudo-first order model: adsorption (A)
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(A)

Figure 6. Pseudo-first order model: electroadsorption (B)
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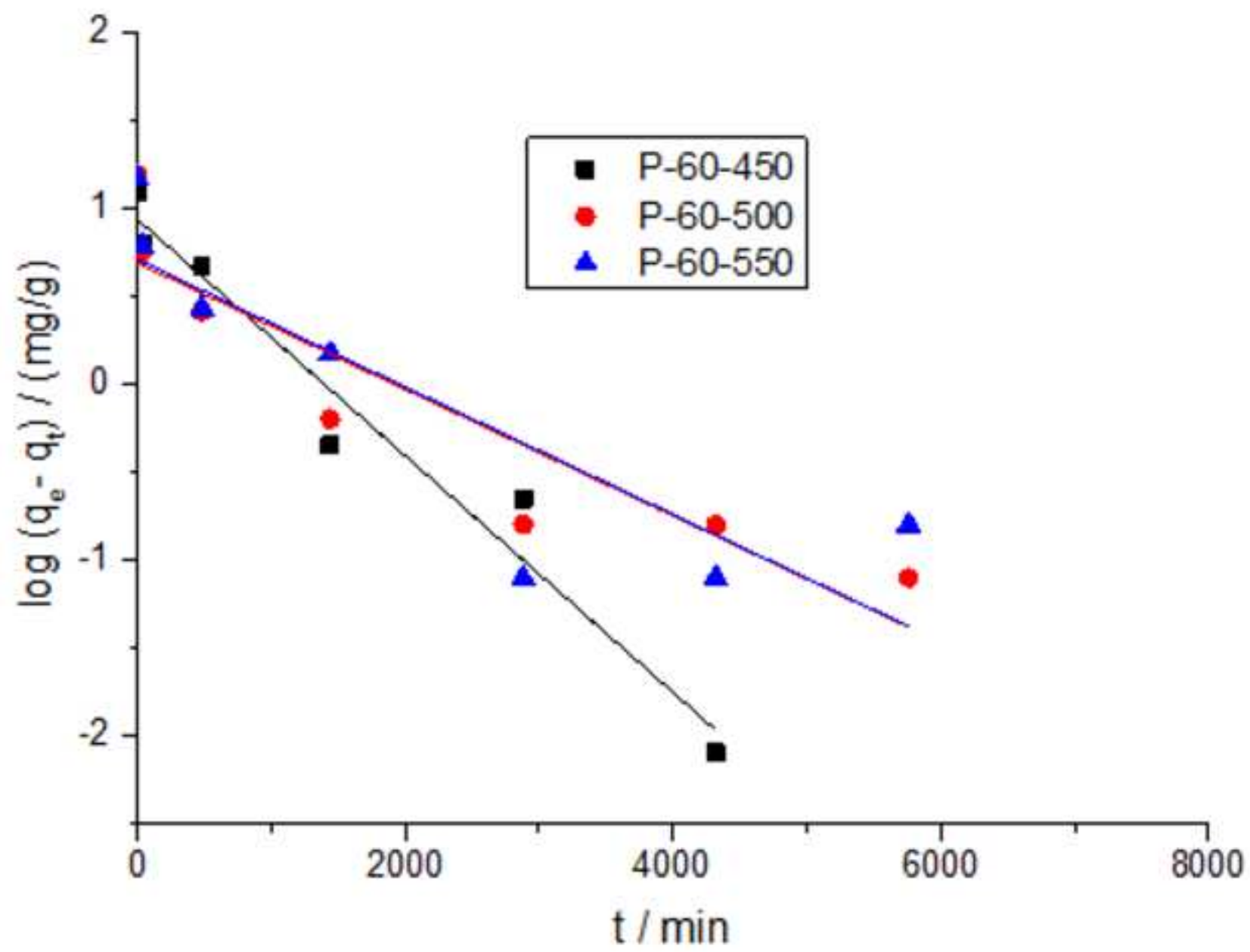


Figure 7: Pseudo-second order model: (A) adsorption
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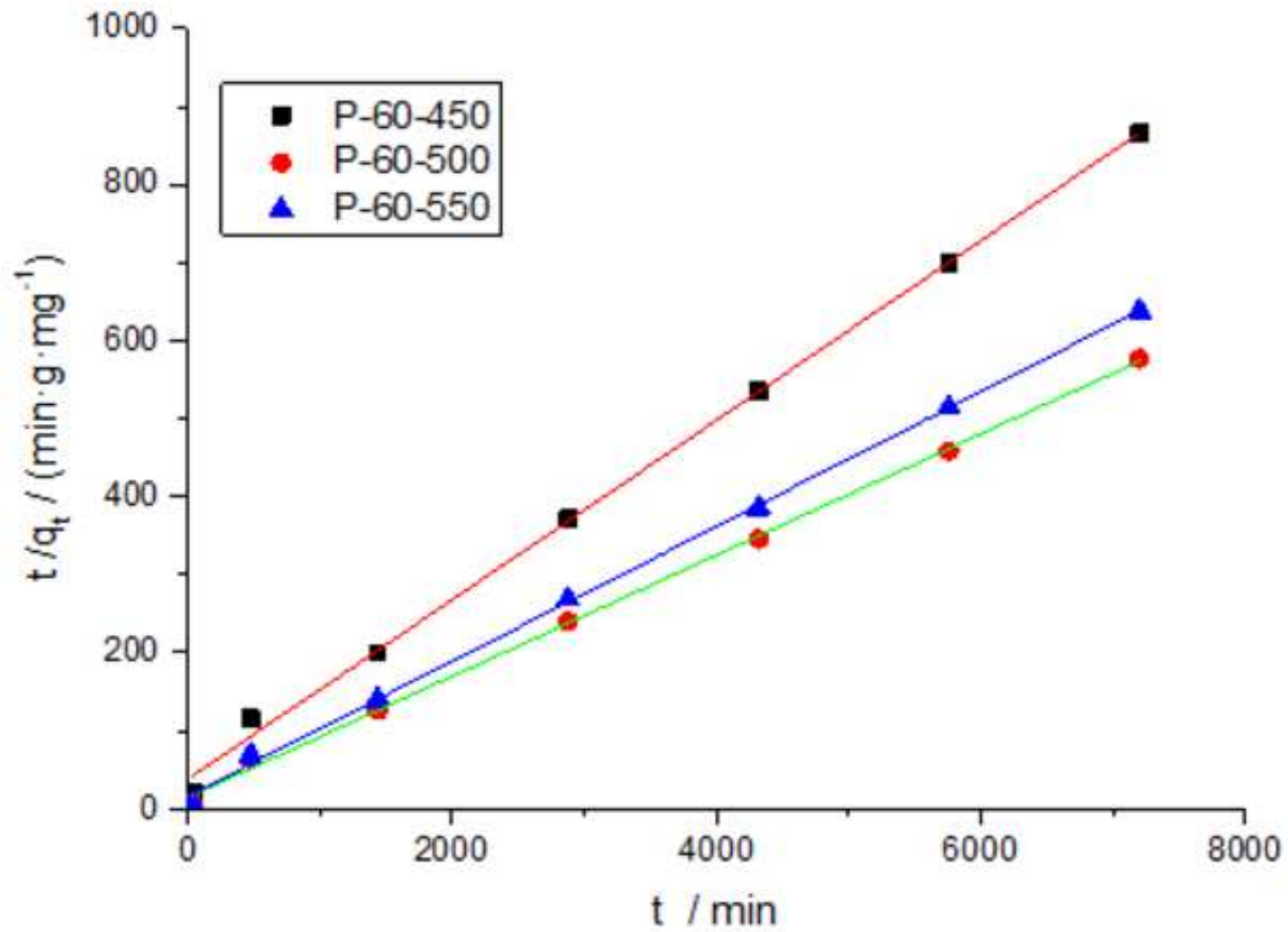
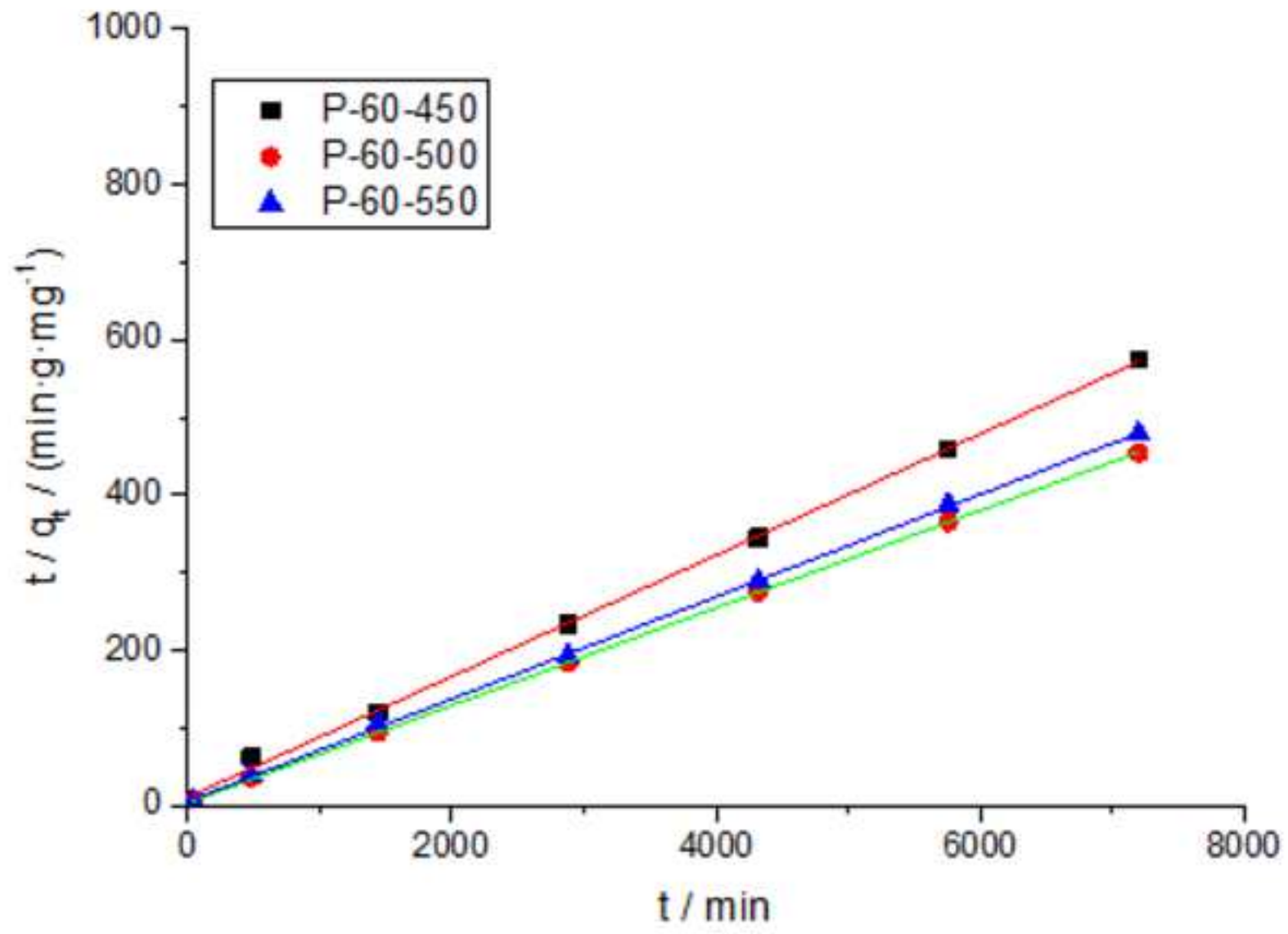
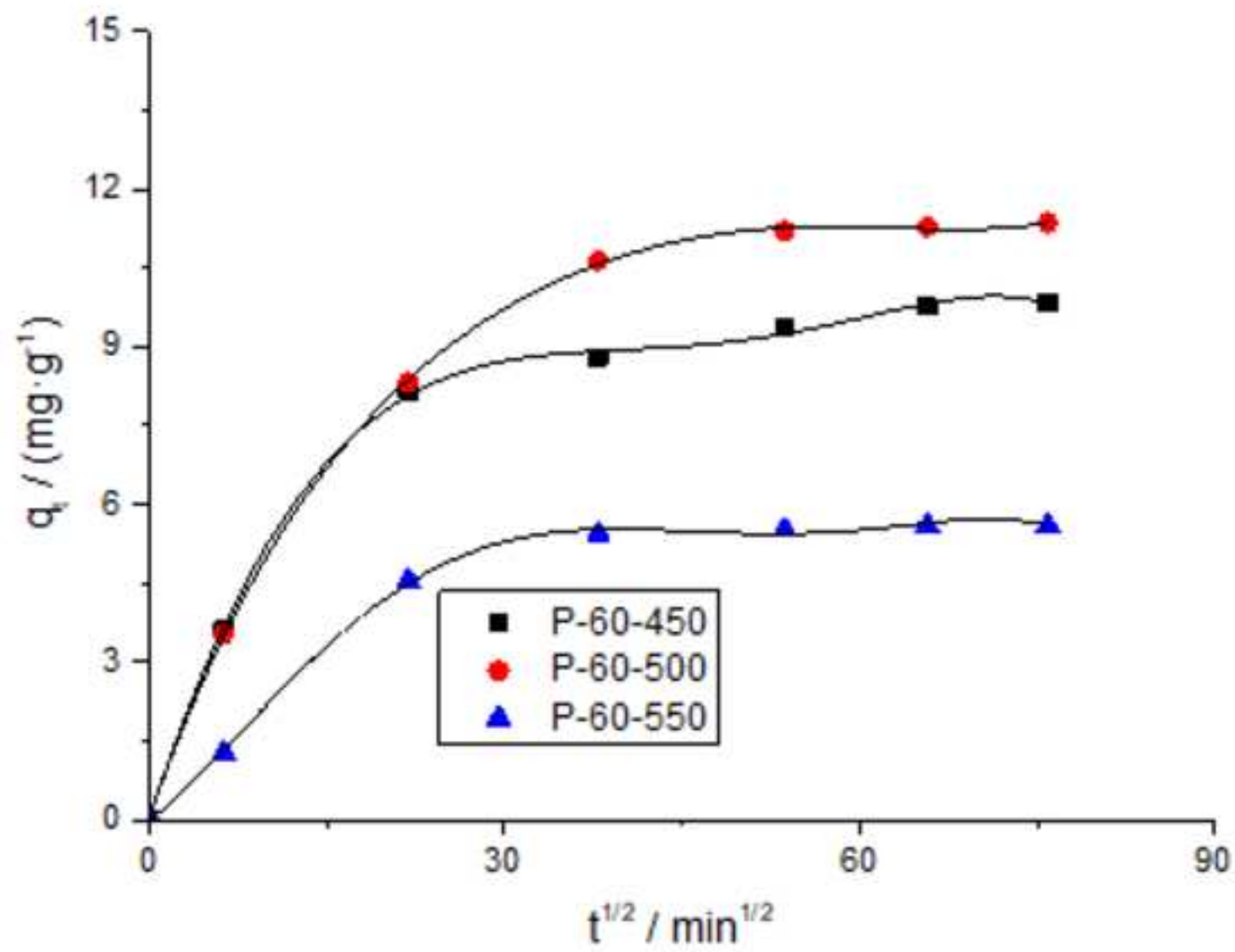


Figure 7: Pseudo-second order model: (B) electro-adsorption
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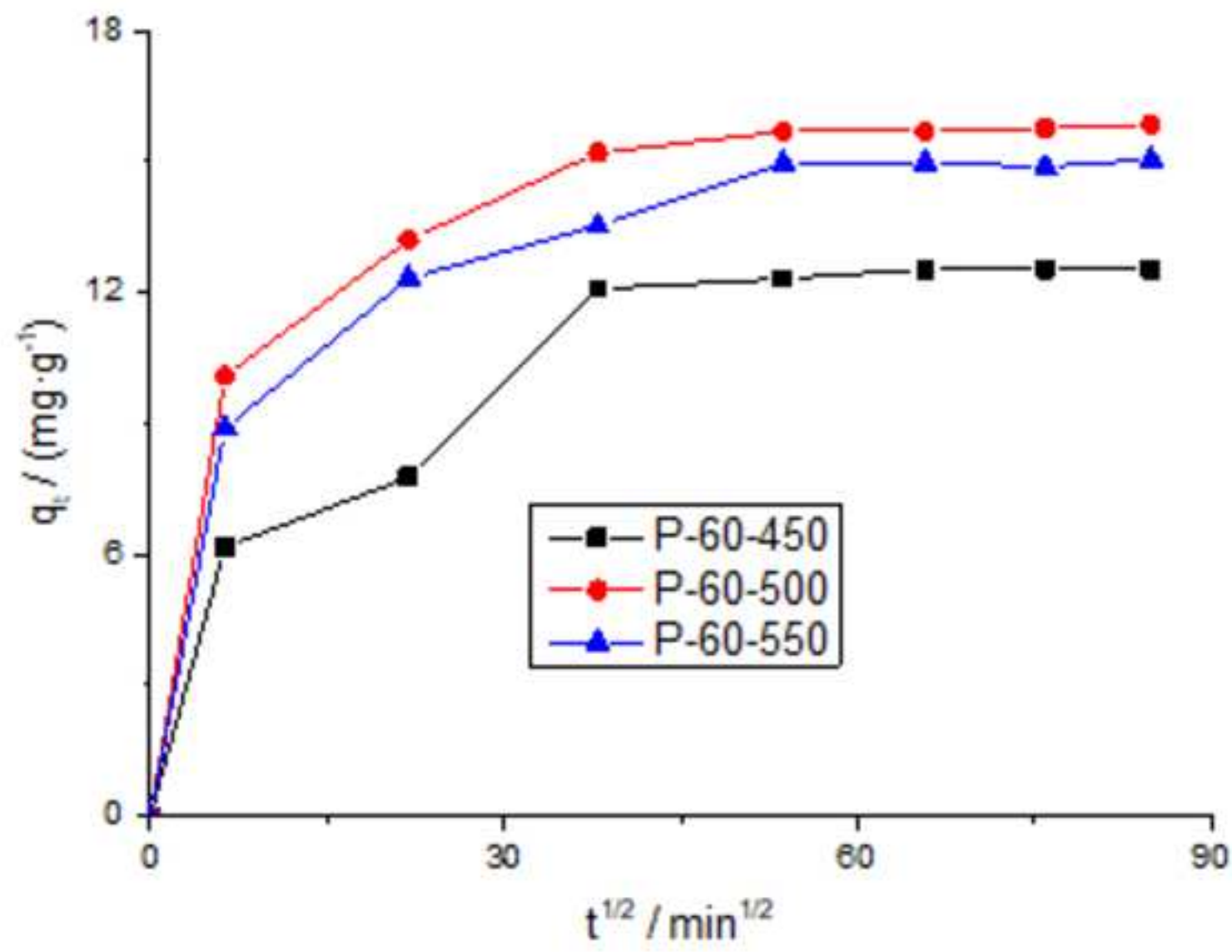
(A)

Figure 8: Intraparticle diffusion model: (A) adsorption
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(A)

Figure 8: intraparticle diffusion model: (B) electro-adsorption
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(B)