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3D Modeling of the Adsorption Rate of Pyridine on Activated Carbon Cloth in a Stirred Tank under Turbulent Conditions

Elias García-Hernández 1*, Carlos Gilberto Aguilar-Madera 2*, Erik Cesar Herrera-Hernández 1, José Valente Flores-Cano 2, Esther Bailón-García 3, Ana Teresa Finol González 2, Angelica Aguilar-Aguilar 1 and Raúl Ocampo-Pérez 1,3

1 Centro de Investigación y Estudios de Posgrado, Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Av. Dr. Manuel Nava 6, Zona Universitaria, San Luis Potosí 78210, Mexico; elias.garcia_hernandez@outlook.com (E.G.-H.); erik.herrera@uaslp.mx (E.C.H.-H.); ma.aguilar@uaslp.mx (A.A.-A.)
2 Facultad de Ciencias de la Tierra, Universidad Autónoma de Nuevo León, Carretera a Cerro Prieto Km 8, Ex-Hacienda de Guadalupe, Liérganes 67700, Mexico; carlos.aguilarmadera@hotmail.com (C.G.A.-M.);
valente.florescn@uantl.edu.mx (J.V.-F.-C.); afinolge@uantl.edu.mx (A.T.F.G.)
3 Departamento de Química Inorgánica, Universidad de Alicante, Carretera de San Vicente s/n, E03080 Alicante, Spain; estherbg@ugr.es

* Correspondence: raul.ocampo@uaslp.mx

Abstract: The experimental and numerical analysis of pyridine adsorption onto activated carbon cloth in a stirred batch adsorber under transition and turbulent regime is presented in this work. Three-dimensional numerical modeling of the adsorption process was implemented for the identification of local velocity, local concentration, and concentration gradients inside the adsorber. This represents a costly computational effort in comparison with conventional batch adsorption models, as for instance the Langmuir kinetic model. Both types of modeling yield comparable results, but the advantage of the 3D modeling is a more detailed resolution of variables, thus avoiding the perfectly mixed assumption. Varying the agitation rate (30–200 rpm) and pyridine initial concentration (99 to 487 mg/L), several kinetic and transport parameters were reported. Hydrodynamic and mass boundary layers are identified around the activated carbon adsorbent following the trajectory of agitation. Furthermore, the major pyridine mass flux takes place around the adsorbent, mainly in the posterior zone regarding the agitation direction. This information is crucial in searching for and designing more efficient and intensive adsorbent systems.

Keywords: 3D modeling; adsorption process; turbulent conditions

1. Introduction

Pyridine is a colorless, unpleasant-smelling organic compound widely used in the dye, pesticide, and herbicide industries and as an intermediate for synthesizing various organic compounds [1]. Because of its high solubility in water, it is present in wastewater from these industries. Pyridine is toxic to humans and has been found to affect organs such as the liver and kidneys and is potentially carcinogenic [1]. Several methods have been proposed to remove pyridine from water, such as: degradation by UV radiation [2,3], electrochemical degradation [4,5], biodegradation with ultrasound waves [6,7], and degradation by gamma radiation [8]. These methods have the disadvantage of generating degradation byproducts with higher toxicity than the original compound due to the low mineralization percentage; additionally, sludge generation as one byproduct is inconvenient [1].

Among the different separation methods, the adsorption process has been shown to be effective, low-cost and easy-to-use for the removal of pyridine from water [9]. Zhu et al. studied pyridine adsorption over two polymeric materials based on polystyrene and divinylbenzene and obtained adsorption capacities up to 85 mg/g at 25 °C [10]. Alonso-Dávila et al. studied the adsorption mechanism of pyridine onto activated carbon cloth...
Processes 2022, 10, 735

(ACC) at pH = 3, 4, 5.2, 6, 8, and 10, while the temperature varied as 15, 25 and 35 °C. The researchers found the maximum adsorption capacity = 70 mg/g under equilibrium concentration of 500 mg/L, and the π-π dispersive interactions played a predominant role during the adsorption at pH between 3 and 6. It was observed that between 15 and 35 °C the adsorption capacity is not affected, which indicates an independent-temperature adsorption process [11]. Mohan et al. studied pyridine adsorption on activated carbon derived from coconut husk waste, reporting adsorption capacities up to 45 and 35 mg/g at 40 and 25 °C, respectively, resulting in an endothermic process. The kinetic study showed that the equilibrium time was reached after 48 h, while the intraparticle diffusion controlled the overall adsorption rate [12].

Focusing over the adsorption kinetics, Ocampo-Pérez et al. [13] elucidated the impact of intraparticle diffusion in the adsorption rate of pyridine on granular activated carbon. The concentration decay curves were interpreted by a diffusional model that considers the pore volume and surface diffusion mechanisms. Interestingly, the researchers demonstrated that surface diffusion is much more important than pore volume diffusion, contributing more than 94% to the total intraparticle diffusion. As pointed out by Ocampo-Pérez and coworkers, the surface diffusion coefficient may be a nonlinear function of the adsorbed mass at equilibrium, and independent of the particle diameter. For the experimental system analyzed, the external mass transport did not affect the overall adsorption rate for agitation rates larger than 150 rpm. Contrarily, for agitation rates below 150 rpm the external mass transport played an essential role on the overall adsorption rate.

The determination of the overall adsorption rate controlling mechanism becomes crucial for the design of large-scale adsorbers. As known, for transport processes in series the slowest stage governs the entire dynamic. The main transport mechanism can be elucidated by applying rigorous mathematical modeling that does not consider the perfect mixing assumption inside the adsorber, i.e., one mathematical model that considers the local concentration and velocity profiles as a function of the stirring velocity. It is not a simple task since it involves the solution of multiple coupled partial differential equations under transient conditions. For example, the Navier–Stokes equation along with the continuity equation must be solved to determine the hydrodynamics in the aqueous system. Additionally, the corresponding convection–diffusion equation must be incorporated in the different phases to evaluate the mass transport. This type of mathematical modeling was recently performed by García-Hernández et al. [14] to evaluate the phenol adsorption on activated carbon felt in a 2D stirred tank. The hydrodynamics were solved considering the laminar regime, while the adsorption process was modeled using a first-order kinetic model at the solid–liquid interface. The results evidenced a good prediction of the experimental data for high and low stirring speeds. In their analysis the Reynolds number varied from 2014 to 13414, indicating transitional and turbulent regime inside the adsorber tank [14]. It was then elucidated that there was a need to implement more rigorous mathematical models for the liquid phase to provide a more appropriate prediction of local velocity and, consequently, improve the prediction of the adsorption rate.

Thus, this work aims to introduce and numerically solve a 3D mathematical model to predict the adsorption rate of pyridine on activated carbon cloth (ACC) in a stirred tank. The mathematical model considers: (i) hydrodynamics in turbulent regime; (ii) convective and diffusive mass transport in the solution; and (iii) adsorption at the solid–liquid interface.

2. Materials and Methods

2.1. Activated Carbon Cloth

The activated carbon cloth (ACC) employed was supplied from Charcoal House. The ACC was washed 5–6 times with deionized water to remove dust and impurities, and then dried at 110 °C during 24 h. Finally, the ACC was stored in a zip lock bag to avoid contamination until further use.

The textural properties of ACC were analyzed by N₂ adsorption at −196 °C using ASAP 2020 equipment from Micrometrics. Previously, the ACC sample was degassed at
100 °C during 12 h under vacuum (≈10^{-2} \text{ Pa}). The specific surface area was calculated by applying the Brunauer–Emmett–Teller (BET) equation to the N\textsubscript{2} adsorption isotherm in the relative pressure range 0.05 ≥ P/P\textsubscript{0} ≤ 0.3. The total micropore volume, W\textsubscript{0}(N\textsubscript{2}), was estimated by applying the Dubinin–Radushkevich equation to the N\textsubscript{2} adsorption isotherm. The mean micropore size (L\textsubscript{0}) for both adsorbates were estimated using the Stoeckli equation. The total pore volume was considered as the volume of N\textsubscript{2} adsorbed at P/P\textsubscript{0} = 0.95. The volume of mesopores (V\textsubscript{meso}) was obtained using the Gurvich rule, and the mean mesopore diameter was calculated by applying DFT calculations.

The ACC morphology was analyzed by scanning electron microscopy (SEM) using a high-resolution SEM microscope, model Helios NanoLab 600 from Thermo Fisher Scientific. The surface chemistry of ACC was characterized by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). The XPS spectra were obtained in a Thermo-Scientific K-Alpha spectrometer using Al-K\textalpha radiation (1486.6 eV). The equipment is equipped with a twin-crystal monochromator, which produces a focused X-ray spot with a diameter of 400 µm. The IR absorption spectra were recorded on a Nicolet 20SXB FTIR spectrometer using KBr/saturated sample pellets. The spectra were recorded in the region of 0–4000 cm\textsuperscript{-1}.

2.2. Adsorbate

The adsorbate used in this work is analytical grade pyridine, which was provided by Fermont Company. The physicochemical properties are presented in Table 1. The solutions were prepared from a 5000 mg/L standard solution. The concentration of pyridine in the solution was determined by UV–visible spectroscopy. The absorbance of a pyridine solution was measured in a spectrometer, Shimatzu model UV-1800, at a wavelength of 249.5 nm. The pyridine concentration was estimated using one absorbance vs. concentration calibration curve, which was prepared from 10 standard solutions with concentrations ranging between 1 and 40 mg/L.

| Compound   | Molecular Structure | Molecular Formula | pK\textsubscript{a} | DAB × 10\textsuperscript{6} cm\textsuperscript{2} s\textsuperscript{-1} | M.W. (g mol\textsuperscript{-1}) | Size X, Y, Z (nm) |
|------------|---------------------|-------------------|---------------------|-----------------------------------|-------------------------------|------------------|
| Pyridine   |                     | C\textsubscript{5}H\textsubscript{5}N | 5.25 | 7.7 | 79.1 | 0.636 | 0.638 | 0.335 |

2.3. Obtaining the Experimental Adsorption Rate

The concentration decay curves were obtained employing one agitated batch adsorber, as shown in Figure 1a. This adsorber consists of a three-hole flat-bottomed flask with a shaft in the center, whose impellers were replaced by two solid-walled stainless-steel cylinders. Then, 1 L of the pyridine solution was placed inside the reactor with initial concentrations between 100 and 500 mg/L, while the impeller cylinders were coated with ACC (1.3 g, approximately). The impeller cylinders were immersed into the pyridine solution, and the agitation was promoted in the range 30–200 RPM. The experiments were kept at pH = 7 and constant temperature = 25 °C; 1 mL aliquots were sampled at different times for determining the concentration until the process reached the equilibrium. In our analysis, the solution volume is considered constant as no more than 3% of the initial volume was removed. The mass of pyridine adsorbed, q(t), as function of time was obtained by the following equation:

\[
q(t) = \frac{V}{m}[C_{A0} - C_A(t)]
\]
where $C_A(t)$ is the pyridine concentration, $C_{A0}$ is the initial pyridine concentration $V$ is the reactor volume, and $m$ is the ACC mass.

![Figure 1. Stirred batch adsorber: (a) 3D geometry, (b) computational domains in the geometry, (c) triangular grid-mesh.](image)

2.4. Mathematical Model

In order to elucidate the most important resistances and dominant mechanisms in the adsorption system, the adsorption rate data were interpreted using two methods: (i) employing the Langmuir kinetic model, and (ii) through the advective–diffusive model coupled to the Langmuir kinetic model considering turbulent flow due the agitation inside the reactor. The basics of these two models are described below.

2.4.1. Fluid Flow Equations

The Reynolds averaged Navier–Stokes equations (RANS) for incompressible and Newtonian fluid describe the hydrodynamics under velocities fluctuations affecting the total flux momentum transport. The average field velocity governing the hydrodynamics in the solution satisfies the following equation:

$$
\frac{\partial}{\partial t}\rho U = -\nabla P - \nabla \cdot (\rhoUU) + \nabla \cdot (\tau^v + \tau^t) + \rho g
$$

Equation (2) must be solved by coupling with the continuity equation and the scheme to evaluate the correlation between velocity fluctuations. The fluid mass balance, also called the continuity equation, describes the spatial variations of fluid density. For a constant fluid density, the mass balance is:

$$
\nabla \cdot U = 0
$$

The Reynolds stress tensor in Equation (2) considers velocity fluctuations and the associated closure due to turbulence in the fluid. Assuming validity of the Boussinesq hypothesis, the Reynolds stress tensor can be equivalently written as the viscous stress tensor according to

$$
\tau^t = -\mu_t \left[ \nabla U + (\nabla U)^T \right] + \frac{2}{3} \kappa I
$$

where $\mu_t$ is the turbulent viscosity and $\kappa$ is the turbulent kinetic energy. Such turbulent parameters are evaluated with the $\kappa - \varepsilon$ model, which consists of the following set of equations:

$$
\rho \frac{\partial \kappa}{\partial t} + \rho (U \cdot \nabla)\kappa = \nabla \cdot \left[ \left( \mu + \frac{\mu_t}{\kappa} \right) \nabla \kappa \right] + P_\kappa - \rho \varepsilon
$$
\[ \rho \frac{\partial \varepsilon}{\partial t} + \rho (U \cdot \nabla) \varepsilon = \nabla \cdot \left[ \left( \mu + \frac{\mu_t}{\sigma_{\varepsilon}} \right) \nabla \varepsilon \right] + C_{\varepsilon 1} \varepsilon P_\kappa - C_{\varepsilon 2} \rho \varepsilon^2 \]  
\[ \mu_t = \rho C_\mu \frac{\kappa^2}{\varepsilon} \]  
\[ P_\kappa = \mu_t \left[ \nabla U : \left( \nabla U + (\nabla U)^T \right) \right] \]  

where \( \varepsilon \) represents the turbulent dissipation of kinetic energy and \( P_\kappa \) quantifies the generation of kinetic energy due to the fluid movement. The set of Equations (2)–(8) helps to solve the momentum transport problem inside the adsorber and allows for obtaining the velocity field that is coupled to the advection–diffusion problem presented below. The solution of this set of equations is complemented with appropriate initial and boundary conditions. The coefficients of the equations above are: \( C_\mu = 0.09 \), \( C_{\varepsilon 1} = 1.44 \), \( C_{\varepsilon 2} = 1.92 \), \( \sigma_\kappa = 1.0 \), \( \sigma_{\varepsilon} = 1.3 \) [15]; they have been widely used for stirred reactors [16,17].

2.4.2. Advective–Diffusive Model (ADM)

The solute transport inside the adsorber is given by the mass balance in the fluid domain considering that Fick’s law is valid. In this way, the pyridine mass transport is given by:

\[ \frac{\partial C_A}{\partial t} - \nabla \cdot (D_{AB} \nabla C_A) + U \cdot \nabla C_A = 0 \]  

where \( D_{AB} \) is the binary (molecular) diffusion coefficient of pyridine in water and \( U \) is the velocity vector given by Equation (2).

Equation (9) is solved assuming that there is no mass flow except for the impellers at the adsorber boundaries, i.e.,

\[ -n \cdot (-D_{AB} \nabla C_A) = 0 \]  

and the initial condition is:

\[ t = 0; \quad C_A = C_{A0} \]  

At the impeller, the following boundary condition applies:

\[ -n \cdot (-D_{AB} \nabla C_A + UC_A) = f(C_A) \]  

This expression means that at the impeller surface the solute mass flux equals the Langmuir-type heterogeneous kinetics; the amount of solute arriving by diffusion and advection to the solution–impeller interface become trapped (disappear) in the cloth as if a superficial reaction takes place.

2.4.3. Langmuir Kinetic Model (LKM)

This model is based on the principles proposed by Langmuir for monolayer adsorption [18,19], where the following equation provides the adsorption rate in the liquid phase:

\[ \frac{dq(t)}{dt} = k_{ad} C_A(t) [q_{im} - q(t)] - k_{des} q(t) \]  

where \( k_{ad} \) and \( k_{des} \) are the adsorption and desorption kinetic constants, respectively. The first term on the right side of Equation (13) represents the adsorption process while the second term represents the desorption process. At equilibrium, the net adsorption rate is equal to zero; therefore, the adsorption rate equals the desorption rate, leading to the following conditions:

\[ \frac{dq(t)}{dt} = 0; \quad q(t) = q_e; \quad C_A(t) = C_{Ae} \]
Substituting Equation (14) into (13) and rearranging the terms, we obtain Equation (15) representing the Langmuir adsorption isotherm:

\[ q_e = \frac{q_m K C_A e}{1 + K C_A e} \]  

(15)

where \( q_m \) is the maximum adsorption capacity and \( K = k_{ad} / k_{des} \) represents the adsorption equilibrium constant.

Introducing mass balance (1), the adsorption rate can be expressed in terms of the concentration. Now, defining \( \alpha = V / m \) and differentiating Equation (1) with respect to time, we have that

\[ \frac{dq}{dt} = -\alpha \frac{dC_A}{dt} \]  

(16)

This result is substituted into Equation (13) along with (1) to obtain:

\[ -\frac{dC_A(t)}{dt} = k_{ad} \left[ C_A(t)^2 + (\beta - C_{A0} + K') C_A(t) - K' C_{A0} \right] \]  

(17)

where \( K' = 1/K \) and \( \beta = q_m / \alpha \). Equation (17) represents the Langmuir kinetic model and is used as boundary condition in Equation (12), i.e.,

\[ f(C_A) = k_{ad} \left[ C_A(t)^2 + (\beta - C_{A0} + K') C_A(t) - K' C_{A0} \right] \]  

(18)

2.4.4. Computational Features

The equations that make up the ADM were solved using the commercial software Comsol Multiphysics, in which the geometry of the adsorber (see Figure 1b) was created by means of two domains: one fixed (external cylinder) and the other rotating (internal cylinder) forming an assembly between both domains. Comsol Multiphysics is based on finite element subroutines where the rotating domain is programmed as a step function at the prescribed agitation rate. Both internal and external domains are coupled by a flow continuity condition for the different physics in the assembly contours. The turbulent \( \kappa - \epsilon \) model was incorporated for the hydrodynamics; meanwhile, the solute mass transport was programmed by means of a general partial differential equation module. The hydrodynamics and mass transport were solved in separate studies using the backward differentiation numerical (BDF) method; both studies were performed using a segregated solver. A tetrahedral array grid mesh was used for the solution (Figure 1c), creating 300791 domain elements, 20690 contour elements, 1616 edge elements, and 76 vertex elements. This grid mesh density is sufficient to yield consistent and accurate results, as compared below with experimental data.

3. Results and Discussion

3.1. Textural, Chemical, and Morphological Characterization of ACC

The morphology of the ACC sample was characterized by SEM and images of the characteristics are depicted in Figure 2. The ACC is made of fibers bundles twined longwise (Figure 2b) of around 0.85 mm, which are threaded crosswise and forming an ordered texture structure (Figure 2a). The magnification of a fiber bundle (Figure 2c,d) reveals that it is formed by individual fibers of about 16.5 \( \mu \)m diameter, which in turn consist of fused individual fibers of 3–4 \( \mu \)m diameter.

The textural properties of ACC were analyzed from N\(_2\) adsorption, displayed in Figure 3. In this isotherm, a type I-B behavior is observed, which is characteristic of microporous materials (a large amount of N\(_2\) is adsorbed at low pressures). Moreover, a slight type H4 hysteresis loop can be observed, which is representative of solids with pores with narrow slits. The experimental data helped to determine that the total pore volume for the material studied was 0.45 cm\(^3\) g\(^{-1}\). The BET equation established a specific area of 880 m\(^2\) g\(^{-1}\), with a micropore volume of 0.44 cm\(^3\) g\(^{-1}\). The pore size distribution presented
in Figure 3 was obtained by the DFT method, a narrow unimodal distribution is observed in the microporous region.

![Microphotographs of the activated carbon cloth: (a) ACC ordered texture structure, (b) fiber bundles twined longwise, (c,d) magnified image of an ACC fiber.](image)

**Figure 2.** Microphotographs of the activated carbon cloth: (a) ACC ordered texture structure, (b) fiber bundles twined longwise, (c,d) magnified image of an ACC fiber.

![N\textsubscript{2} adsorption–desorption isotherm and (b) pore size distribution.](image)

**Figure 3.** (a) \(\text{N}_2\) adsorption–desorption isotherm and (b) pore size distribution.

The surface chemistry was analyzed by XPS and FTIR. \(\text{C}_{1s}\), \(\text{O}_{1s}\), and \(\text{N}_{1s}\) spectral regions are depicted in Figure 4 and data by deconvolution of these regions are collected in Table 2. The \(\text{C}_{1s}\) spectral region can be fitted using six peaks: at 284.6 eV attributed to nonoxygenated amorphous carbon, at 285.6, 286.3, 287.3, and 288.9 eV assigned to alcohol and ether (C-O), carbonyl (C=O), carboxyl (COO\textsuperscript{-}), and carbonate groups, respectively, and a weak peak found at 291.4 eV assigned to \(\pi\)-plasmon excitations. In turn, the \(\text{O}_{1s}\) region shows three peaks centered at 531.5 eV, characteristic either of a bonded hydroxyl group (–OH) or oxygenated
groups such as ketones (C=O) on the carbon surface [20]; at 532.7 eV which corresponds to acids, anhydrides, lactones, or ether groups (C–O–C), and at 533.7 ascribed to chemisorbed oxygen. The N$_{1s}$ spectral region shows four types of nitrogen functionalities: pyridinic-N (N-6) at 398.3 eV, pyrrolic-N or pyridone-N (N-5) at 400.3 eV, and quaternary nitrogen (N-Q) at 401.4 eV, and N-oxide at 403.2 eV. Analyzing the surface composition of the sample, the ACC surface is composed of 16.8 wt.% O and 1.1 wt.% N.

The surface chemistry was also characterized by FTIR and data are collected in Figure S1 (Supplementary Materials). The peaks at 670 and 1050 cm$^{-1}$ are assigned to the aromatic ring’s presence. The bands at about 1165 and 1230 cm$^{-1}$ can be assigned to the stretching modes of the C–O species in acids, esters, or ethers [20]. The band at around 1390 cm$^{-1}$ indicates the presence of nitrogen species C–N in the carbon structure, which corroborate the results of the XPS. The band at 1725 cm$^{-1}$ can be assigned to the stretching vibration of C=O in carboxylic acid and lactone group. Note also that an intense band appears at 2325–2368 cm$^{-1}$, ascribed to the –OH bond pertaining to carboxylic groups [21]. The bands at 2890 and 2970 cm$^{-1}$ are assigned to the stretching modes of C–H bonds.

### 3.2. Adsorption Equilibrium

Seventeen experiments were conducted by varying the agitation rate at 30, 50, 100, 150, and 200 rpm, in order to determine the effects of agitation on the concentration decay curves. The initial pyridine concentration was varied between 100 and 500 mg/L at agitation rates of 30, 100, and 200 rpm. All the experimental runs were further simulated by employing the LKM and ADM formulations, where the parameters $k_{ad}$ and $k_{ad}'$ need to be optimized to match the experimental curves. Features of the experimental runs are summarized in Table 3, together with the values of various parameters. Within the optimization procedure for model

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**Figure 4.** (a) $C_{1s}$, (b) $O_{1s}$, and (c) $N_{1s}$ spectral regions of ACC.

**Table 2.** XPS results of ACC: the C, O, and N surface contents ($C_{XPS}$, $O_{XPS}$, and $N_{XPS}$), binding energy, and percentage of the components used to fit the $C_{1s}$, $O_{1s}$, and $N_{1s}$ spectral regions.

| Sample | BE (eV) | $C_{1s}$ Peak % | BE (eV) | $O_{1s}$ Peak % | BE (eV) | $N_{1s}$ Peak % | $C_{XPS}$ %Wt | $O_{XPS}$ %Wt | $N_{XPS}$ %Wt |
|--------|---------|----------------|---------|----------------|---------|----------------|-------------|-------------|-------------|
| ACC    | 284.6   | 61             | 531.5   | 25             | 398.3   | 25             | 82.1        | 16.8        | 1.1         |
|        | 285.6   | 17             | 532.7   | 55             | 400.3   | 34             |             |             |             |
|        | 286.3   | 7              | 533.7   | 20             | 401.4   | 30             |             |             |             |
|        | 287.3   | 5              |         |                | 403.2   | 30             |             |             |             |
|        | 288.9   |                |         |                |         | 11             |             |             |             |
|        | 290.9   | 4              |         |                |         |                |             |             |             |

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parameters, the following percentage deviation needs to be minimized. Here, $q_i^{\text{obs}}$ represents the experimental data and $q_i^{\text{pred}}$ the data predicted from the mathematical model:

$$\%D = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{q_i^{\text{obs}} - q_i^{\text{pred}}}{q_i^{\text{obs}}} \right| \times 100$$ (19)

Table 3. Kinetic parameters and experimental conditions used to obtain the adsorption rate of pyridine on ACC.

| No. | EXP | RPM | C$_{A0}$ mg L$^{-1}$ | $q_{e,\text{exp}}$ mg g$^{-1}$ | LKM | ADM |
|-----|-----|-----|-----------------------|-------------------|-----|-----|
|     |     |     |                       |                   | $q_e$ cal mg g$^{-1}$ | $k_{ad} \times 10^4$ L mg$^{-1}$ s$^{-1}$ | %D | $q_e$ cal mg g$^{-1}$ | $k_{ad}'$ cm$^3$ mg$^{-1}$ s$^{-1}$ | %D |
| 1   | 30  | 487 | 120                   | 119               | 2.86 | 0.7 | 118 | 0.0135 | 1.2 |
| 2   | 50  | 487 | 120                   | 119               | 5.49 | 4.6 | 119 | 0.018  | 1.2 |
| 3   | 100 | 487 | 120                   | 119               | 11.3 | 1   | 119 | 0.017  | 4.1 |
| 4   | 150 | 487 | 120                   | 118               | 17.02| 6.3 | 119 | 0.02   | 1.4 |
| 5   | 200 | 487 | 120                   | 121               | 14.9 | 4.9 | 120 | 0.025  | 0.9 |
| 6   | 30  | 99  | 47                    | 44                | 2.44 | 4.9 | 46  | 0.118  | 5.6 |
| 7   | 30  | 198 | 71                    | 71                | 6.09 | 1.4 | 72  | 0.01   | 3.5 |
| 8   | 30  | 295 | 98                    | 99                | 2.78 | 0.5 | 98  | 0.0125 | 3.4 |
| 9   | 30  | 385 | 108                   | 105               | 0.73 | 1.7 | 108 | 0.011  | 2.7 |
| 10  | 100 | 99  | 47                    | 48                | 7.66 | 1.4 | 48  | 0.018  | 6.7 |
| 11  | 100 | 198 | 71                    | 72                | 7.68 | 3.2 | 73  | 0.017  | 6.5 |
| 12  | 100 | 295 | 98                    | 95                | 9.16 | 1.3 | 95  | 0.019  | 4.9 |
| 13  | 100 | 385 | 108                   | 106               | 6.58 | 0.8 | 107 | 0.018  | 2.6 |
| 14  | 200 | 99  | 47                    | 46                | 20.9 | 7.2 | 47  | 0.0255 | 5.6 |
| 15  | 200 | 198 | 71                    | 73                | 12.5 | 3.8 | 72  | 0.021  | 3.5 |
| 16  | 200 | 295 | 98                    | 96                | 14.7 | 2.6 | 95  | 0.0225 | 3  |
| 17  | 200 | 385 | 108                   | 106               | 16.3 | 3.3 | 107 | 0.0211 | 2.7 |

3.3. Analysis with the Langmuir Kinetic Model (LKM)

Adsorption equilibrium data were obtained at different initial concentrations and then used to build the Langmuir isotherm given by Equation (15). The Langmuir isotherm was fitted using the STATISTICA software by minimizing the objective function

$$E(k_{ad}, k_{ad}') = \frac{1}{2} \sum_{i=1}^{N} \left( q_i^{\text{obs}} - q_i^{\text{pred}}(k_{ad}, k_{ad}') \right)^2.$$ 

The experimental data and the mathematical predictions, together with the fitted parameters are reported in Figure S2. In general, the Langmuir model predicts equilibrium concentrations well, with an error under 5%. Further, the Langmuir isotherm parameters are used in the LKM and ADM models to adjust to the experimental decay curves.

Figure 5 shows the adsorption rate curves for experiments (Exps.) 1–5 at different stirring rate. It is observed that the adsorption capacity is similar for all the experiments, around 120 mg/g; nevertheless, the effect of hydrodynamics on each adsorption rate curve is different when the equilibrium time is analyzed; the equilibrium is reached slowly for those experiments at small agitation rates and the opposite is observed for agitation rate cases. For instance, Exp. 5 carried out at 200 rpm reached equilibrium after approximately 50 min, while Exp. 1 at 30 rpm met the equilibrium around 210 min, i.e., three times longer than the case of Exp. 5. For Exps. 2, 3, and 4, the adsorption equilibrium was reached near 180, 150, and 90 min, respectively.
In Figure 5, predictions of the LKM are outstanding for Exps. 1–5 at 120 mg/g of equilibrium concentration. The adjusted parameter $k_{ad}$ ranged from $2.86 \times 10^{-4}$ to $17.02 \times 10^{-4} \text{ L/(mg s)}$. The maximum value for $k_{ad}$ was found at 150 rpm and then decreased for 200 rpm. The minimum $k_{ad}$ corresponds for 30 rpm. Considering that the LKM does not consider the mass transport in the solution, but only the adsorption on the active sites of the adsorbent, and then none of the parameters quantify the hydrodynamics. Thus, such phenomenon is implicitly included in the variations of the kinetic constant $k_{ad}$. This can explain why the parameter $k_{ad}$ varies if the agitation rate changes. For the experiments plotted in Figure 5, the percentages of deviation obtained from the Equation (19) are collected in Table 3; all are less than 5% except for Exp. 4. ($\%D = 6.3$), so we can argue that the LKM predicts the experimental adsorption rate data reasonably well.

In Figure S3, we plot the adsorption rate at different initial concentrations ranging from 99 to 487 mg/L, fixing the agitation rate at 30 rpm. The initial concentration plays a key role in the adsorption equilibrium; the higher the initial concentration, the faster the equilibrium is reached. In Figure S3, Exp. 1 (initial concentration = 487 mg/L) reaches equilibrium after approximately 210 min, while the Exp. 6 (initial concentration = 99 mg/L) takes more than 300 min to reach equilibrium. The higher concentration between the solution and the surface of the adsorbent material gradient explains this effect, as this generates a faster mass flux towards the carbon cloth. The fitted parameter $k_{ad}$ ranges from $0.73 \times 10^{-4}$ to $6.09 \times 10^{-4} \text{ L/(mg s)}$ in these cases. According to Table 3, the parameter $k_{ad}$ appears to be constant around $2.7 \times 10^{-4} \text{ L/(mg s)}$ for Exps. 1, 6, and 8, which may denote the effect of the initial concentration while fixing the agitation rate. Based on the percentage deviation calculations, we state that LKM interprets well the experimental data.

In Figures S4 and S5, the effect of the initial concentration on the adsorption capacity is analyzed at 100 and 200 rpm, respectively. It is observed that the adsorbed pyridine at equilibrium is the same as for the corresponding cases in Figure S3. This means physically that the adsorption equilibrium is independent of the agitation rate, but it depends significantly on the initial concentration of solute. Comparing the Exp. 10 (S4) and 14 (S5) (both at initial concentration = 99 mg/L), note that the adsorption rate is affected by the agitation rate, as there is a difference of around 80 min to reach equilibrium; in other words, the adsorption process at 100 rpm is 1.6 times slower than that for 200 rpm. The same effect is observed when comparing the pairs of Exps. 11 and 15, 12 and 16, 13 and 17, and 3 and 5,
whose initial concentrations are 198, 295, 385, and 487 mg/L, respectively. In those cases, the time necessary to reach the equilibrium ranged from 80 to 120 min for the experiments with higher initial concentrations.

3.4. Analysis with the Adective Diffusive Model (ADM)

As discussed above, we solved the ADM using a 3D geometry representing a highly intensive computational procedure. It is the main reason why such a modeling method is not commonly used to simulate adsorption experiments. In this case, we performed numerical simulations for agitation rates: 30, 50, 100, 150, and 200 rpm that, according to the Reynolds number definition in Equation (20), the flow regime is classified as transition for 30, 50, 100 rpm, while turbulent conditions are met for 150 and 200 rpm. For the turbulent regimes, it is necessary to incorporate the turbulent viscosity and additional equations accounting for the kinetic energy and dissipation rate. Thus, the RANS model is employed within the Comsol software environment. We recall that we are dealing with the calculation of local velocities and pressure within the agitated adsorber, and furthermore, higher resolutions of flow paths, concentration, and mass fluxes can be provided via the solution of the ADM. In Equation (20), \( Nr \) represents the stirring speed and \( D \) the impeller diameter.

\[
\text{Re} = \frac{\rho Nr D^2}{\mu}
\]  

In Figure 6a, we plot the local velocity in the fluid at five x–y cutting planes for the case of 100 rpm. The largest velocity takes place in the vicinity of the impellers for the upper and lower parts of the adsorber where the maximum velocities are similar. The zone with the lowest velocity is that in the center of the adsorber, which is due to the geometrical arrangement of the impeller shaft. Interestingly, in Figure 6a, hydrodynamic boundary layers can be observed around the adsorbent ACC, mainly following the angular path driven by the agitation arrangement. This arrangement contributes to homogenize, in some degree, the local velocity inside the adsorber. This can be verified with the cutting plane plots and the velocity vectors represented by the red arrows shown in Figure 6b, where the lengths of these vectors are quite similar and they increase close to the adsorber impellers. Another important variable we plot are the local streamlines of fluid, which help us to determine the trajectory followed by the fluid molecules. The streamlines are plotted in Figure 6c; these lines follow a complete distribution inside the adsorber with trajectories along all directions. This means that the use of the hydrodynamic model can elucidate the behavior of the fluid where the velocity of a fluid element varies both in magnitude and position inside the adsorber.

![Figure 6. Hydrodynamic variables in the adsorber at 100 rpm: (a) velocity profiles (cm/s) in x–y planes, (b) proportional local velocity vectors, (c) streamlines.](image-url)
The streamlines of flow also contribute to determining the time when the steady state is reached, and this happens when the elements of the fluid passing through a given x–y–z coordinate follow the same trajectory as time passes; we then say that the hydrodynamic equilibrium is met inside the adsorber. Reaching hydrodynamic equilibrium does not mean that mass equilibrium is also achieved. The dynamics of both phenomena are decoupled and governed by different physical parameters and time scales; hydrodynamic equilibrium takes place in a short period compared to mass equilibrium. One visual and quantitative manner to verify the hydrodynamic equilibrium is by plotting the average velocity of the entire adsorber versus the time and see no changes in the average velocity after a period. This fact is observed in the plots of Figure S6a; there we notice that the equilibrium time depends on the agitation rate: the higher the agitation rate, the faster the equilibrium is reached. According to results plotted in Figure S6a, the hydrodynamic equilibrium at 30, 50, 100, 150, and 200 rpm is obtained after 25, 20, 15, 12, and 10 s, respectively; the steady-state average velocity for each case is 2.5, 4.5, 10.5, 16, 23 cm/s, respectively. Note that the steady-state average velocity grows to a lesser extent while the agitation speed increases. At a high level of agitation, the fluid loses momentum through turbulent dissipation. Thus, a certain amount of mechanical energy transmitted by the impeller to the liquid is dissipated by the turbulence. These results of the local velocity inside the adsorber help to further elucidate the main mechanisms for transport and adsorption of pyridine.

Figure S6b shows the time evolution of the turbulent kinetic energy as a function of the agitation rate. As observed, the hydrodynamic equilibrium coincides approximately with a constant behavior of parameter \( \kappa \) with time, and one can conclude that the kinetic energy also reaches equilibrium. Such energetic equilibrium is reached faster for high stirring speeds than for slow cases. For instance, at 30 rpm the kinetic energy becomes constant after 20 s, while for 200 rpm the invariance over time takes place after approximately 10 s. In Figure S6b, another interesting feature can be observed: increasing the agitation rate yields larger kinetic energy inside the adsorber. The increase in the turbulent kinetic energy could imply a major number of vortices inside the adsorber; physically, this can be synonyms of better mixing at higher rpm and, therefore, a major homogeneity of solute inside the adsorber. Notice how, as the stirring rate increases inside the adsorber, the kinetic energy also exponentially increases. For instance, the kinetic energy at 200 rpm is 25 times higher than that for 30 rpm. However, here it is worth mentioning that higher agitation rates could create better mixing conditions from the point of view of local velocities and turbulent kinetic energy, but that also means that major power consumption must be provided through the stirring rotor, thus increasing the operation costs at industrial levels. The analysis of the turbulent kinetic energy is accompanied by the dissipation energy term \( \epsilon \), which is plotted in Figure S6c as function of the agitation rate. As expected, increasing the agitation rates indicates that more energy is dissipated into the vortices formed in the fluid.

Figure 7 shows the effect of the agitation rate on the adsorption capacity of pyridine on activated carbon cloth at an initial concentration of 487 mg/L. The maximum mass capacity found for pyridine adsorption at equilibrium is 120 mg/g. The curves plotted in Figure 7 correspond to results from the solution of the ADM described in the sections above. For Exps. 1 to 5, the mathematical model predicts accurately the adsorption equilibrium and, according to Table 3, the percentage of deviation of the model with respect to the experimental data is less than 5%. From these observations, it can be asserted that the ADM predicts well the equilibrium and kinetic data.

Figure 8 presents the adsorption kinetics at different initial concentrations while fixing the agitation rate at 30 rpm. The dotted curves represent the numerical predictions by the ADM for experiments 1 and 6 to 9. It is observed that the model accurately predicts the adsorption equilibrium for all the cases. However, a slight mismatch with experimental data at about 30 min can be seen in Exps. 6 and 7. These experiments correspond to lower initial concentrations. Because this mismatch does not appear for higher initial concentrations (Exps. 1, 8, and 9), it can be said that the prediction capability of the ADM predictions is affected by the initial concentrations at low stirring revolutions. One
A possible explanation for this phenomenon is that the concentration gradient between the solution and the adsorbent surface is too small, and the model does not estimate them correctly at early times. According to data reported in Table 3, the values of parameter $k_{ad}'$ are in the range $0.01$ to $0.1 \text{ cm}^4 \text{ mg}^{-1} \text{ s}^{-1}$, and the percentages of deviation with respect to experimental data are less than $5\%$, except for Exp. 6 whose deviation is $5.6\%$. In this regard, even with that small deviation shown in Exps. 6 and 7, the model can be used to interpret the kinetic data.

Figure 7. Variation in ACC adsorption capacity as a function of the agitation rate. Predictions from the advection–diffusion model are represented by dashed lines, while the discrete values correspond to experimental data.

Figure 8. Variation in ACC adsorption capacity as a function of the mass of pyridine adsorbed. Predictions from the advection–diffusion model are represented by dashed lines, while the discrete values correspond to experimental data.

Figures S7 and S8 show the effect of the initial concentration at 100 and 200 rpm, respectively. For both figures, the predictions made by the ADM are close to the equilib-
rium and experimental data with deviation percentages close to 5% (see Table 3). When comparing both figures, it is noted that the agitation rate plays an important role in the adsorption rate. We recall that the agitation rate significantly changes the hydrodynamics, affecting the local mass flux around the carbon cloth. This phenomenon is reflected in the physical parameters involved in any mathematical model. For instance, note the variations of parameter $k_{ad}'$ at different initial concentrations. The adjustment of this parameter helps to interpret the experimental data correctly in the 3D numerical simulation, where the local mass fluxes and concentrations can be accurately computed. Here, the 3D simulation capabilities are highlighted, since, in this way, a more significant physical meaning of interpreted results is elucidated.

One 3D numerical simulation based on the ADM formulation allows for observing how the adsorption process takes place from the solution to the surface of the adsorbent material. This type of modeling calculates the local concentration gradients in every point inside the adsorber, as well as the pyridine mass flux. From the analysis presented below, we corroborate for all the agitation rates studied that convection is the dominant mechanism for solute transport in the solution and to the adsorbent surface. For instance, we plot in Figure 9 the concentration gradients at different times for Exp. 3 (initial concentration $= 487$ mg/L at 100 rpm). Theoretically, at the beginning of simulations, $t = 0$ min, there are no pyridine concentration gradients in the solution (Figure 9a) because the adsorption process has not yet started. As soon as the adsorption and agitation start, concentration gradients are created in the solution (Figure 9b) for $t = 5$ min in different zones. The smaller concentrations take place close to the surface of the driving cylinders coated with the ACC. It is clear that the adsorption promotes the concentration gradients; in fact, for $t = 5$ min, mass boundary layers can be observed around the ACC following the angular trajectory in a similar manner as the case of the hydrodynamic boundary layer (see Figure 6a). The concentration gradients are significant until the equilibrium is reached, as shown in Figure 9c, where the concentration is practically homogeneous at $t = 210$ min.

The analysis of pyridine mass flux in the fluid solution is visually presented in Figure 10. In this case, we plotted the total mass flux vector:

$$N = U C_A - D_{AB} \nabla C_A$$

Owing to the agitation, the convective contribution is much more significant than the transport by diffusive mechanism. It is evident in the flux vectors as they follow the trajectory of the fluid movement. One relevant finding is that the largest mass flux takes place in the rear of driving cylinders, while in the fluid bulk (far from the static boundaries) the mass flux is smaller. We noticed from the vector velocity plotted in Figure 10b that the
major contributions of velocity are in the radial and angular directions rather than in the axial direction.

A comparison between the values of the LKM- and ADM-fit constants allows us to corroborate that when the kinetic model does not depend directly on the agitation conditions within the system, its constants take on greater physical significance as they depend directly on the adsorption conditions such as initial concentration and thus the adsorption capacity; therefore, the ADM model allows a better understanding of the system studied (see Figure S9).

Figure 10. (a) Concentration profile and mass fluxes. (b) Zoom in the lower ACC. Agitation rate = 100 RPM, initial concentration = 487 mg/L, simulation time = 1 min.

4. Conclusions

We employed mathematical modeling for the pyridine adsorption onto activated carbon cloth in one agitated batch adsorber. The mathematical model is composed of a turbulent momentum balance equation in the solution, the solute mass balance, and ancillary expressions to model the adsorption onto the carbon surface. The solution of the mathematical model is carried out numerically in one 3D environment where the activated carbon cloth rotates around the central axis of the adsorber. Computationally, this represents a challenging task compared to traditional adsorption models where all the dynamics of transport and adsorption of solute is modeled through kinetic expressions, which assume the perfect mixing condition in the solution. It was corroborated that this type of modeling can predict well the decay curves of concentration in the solution for various agitation rates (from 30 to 200 rpm) and initial concentrations of pyridine (from 99 to 487 mg/L). The accuracy of the numerical predictions of decay curves is comparable with those obtained from the Langmuir kinetic model. Some of the capabilities of our 3D mathematical model are the possibilities to compute accurately the local solute mass flux around the carbon cloth and the local concentrations as functions of time and position. We identify that, depending on the agitation rate, the assumption of a perfect mixing condition is questionable over some process periods. Additionally, we did observe the existence of mass and hydrodynamic boundary layers around the adsorbent material following the angular direction.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr10040735/s1, Figure S1: The FTIR spectra of activated carbon cloth ACC; Figure S2: Adsorption equilibrium data for pyridine. The symbols represent the experimental data and the solid line the predictions of the Langmuir isotherm model; Figure S3: Variation in the adsorption capacity of ACC as a function of the mass of adsorbed pyridine at 30 rpm. The predictions of the Langmuir kinetic model are represented by dashed lines, while the discrete values correspond to experimental data; Figure S4: Variation in ACC adsorption capacity as a function of the mass of adsorbed pyridine at 100 rpm. The predictions of the Langmuir kinetic model are
represented by dashed lines, while the discrete symbols correspond to experimental data; Figure S5: Variation in ACC adsorption capacity as a function of the mass of adsorbed pyridine at 200 RPM. The predictions of the Langmuir kinetic model are represented by dashed lines, while the discrete symbols correspond to experimental data; Figure S6: (a) Average velocity (cm/s) vs. time (s) as a function of the agitation rate. (b) Kinetic energy turbulence (cm\(^2\)/s\(^2\)) vs. time (s) as function of the agitation rate. (c) Turbulence dissipation rate (cm\(^2\)/s\(^3\)) vs. time (s) as a function of stirring speed; Figure S7: Variation in ACC adsorption capacity as a function of the mass of pyridine adsorbed. Here, the agitation rate is 100 rpm. Predictions from the advection–diffusion model are represented by dashed lines, while the discrete values correspond to experimental data; Figure S8: Variation in ACC adsorption capacity as a function of the mass of pyridine adsorbed. Here, the agitation rate is 200 rpm. Predictions from the advection–diffusion model are represented by dashed lines, while the discrete values correspond to experimental data; Figure S9: Comparison between the adjustment constants (a) ADM and (b) LKM.

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**References**

1. Padoley, K.V.; Mudliar, S.N.; Pandey, R.A. Heterocyclic nitrogenous pollutants in the environment and their treatment options—An overview. *Bioresour. Technol.* 2008, 99, 4029–4043. [CrossRef] [PubMed]

2. Liu, T.; Ding, Y.; Liu, C.; Han, J.; Wang, A. UV activation of the pi bond in pyridine for efficient pyridine degradation and mineralization by UV/H2O2 treatment. *Chemosphere* 2020, 258, 127208. [CrossRef] [PubMed]

3. Liu, S.; Han, J.; Ding, Y.; Gao, X.; Cheng, H.; Wang, H.; Liu, C.; Wang, A. Advanced reduction process to achieve efficient degradation of pyridine. *Chemosphere* 2022, 287, 132240. [CrossRef] [PubMed]

4. Li, D.; Tang, J.; Zhou, X.; Li, J.; Sun, X.; Shen, J.; Wang, L.; Han, W. Electrochemical degradation of pyridine by Ti/SnO\(_2\)/Sb tubular porous electrode. *Chemosphere* 2016, 149, 49–56. [CrossRef]

5. Lou, Z.; Song, Y.; Shao, B.; Hu, J.; Wang, J.; Yu, J. Pre-electrochemical treatment combined with fixed bed biofilm reactor for pyridine wastewater treatment: From performance to microbial community analysis. *Bioresour. Technol.* 2021, 319, 124110. [CrossRef]

6. Lu, Q.; Zhang, Y.; Li, N.; Tang, Y.; Zhang, C.; Wang, W.; Zhou, J.; Chen, F.; Rittmann, B.E. Using ultrasonic treated sludge to accelerate pyridine and p-nitrophenol biodegradation. *Int. Biodeterior. Biodegrad.* 2020, 153, 105051. [CrossRef]

7. Zhu, G.; Xing, F.; Tao, J.; Chen, S.; Li, K.; Cao, L.; Yan, N.; Zhang, Y.; Rittmann, B.E. Synergy of strains that accelerate biodegradation of pyridine and quinoline. *J. Environ. Manag.* 2021, 285, 112119. [CrossRef]

8. Chu, L.; Yu, S.; Wang, J. Degradation of pyridine and quinoline in aqueous solution by gamma radiation. *Radiat. Phys. Chem.* 2018, 144, 322–328. [CrossRef]

9. Daware, G.B.; Gogate, P.R. Removal of pyridine using ultrasound assisted and conventional batch adsorption based on tea waste residue as biosorbent. *Environ. Technol. Innov.* 2021, 21, 101292. [CrossRef]

10. Zhu, Q.; Moggridge, G.D.; Ainte, M.; Mantle, M.D.; Gladden, L.F.; D’Agostino, C. Adsorption of pyridine from aqueous solutions by polymeric adsorbents MN 200 and MN 500. Part 1: Adsorption performance and PFG-NMR studies. *Chem. Eng. J.* 2016, 306, 67–76. [CrossRef]

11. Alonso-Davila, P.; Torres-Rivera, O.; Leyva-Ramos, R.; Ocampo-Perez, R. Removal of Pyridine from Aqueous Solution by Adsorption on an Activated Carbon Cloth. *Clean Soil Air Water* 2012, 40, 45–53. [CrossRef]
12. Mohan, D.; Singh, K.P.; Sinha, S.; Gosh, D. Removal of pyridine from aqueous solution using low cost activated carbons derived from agricultural waste materials. *Carbon* **2004**, *42*, 2409–2421. [CrossRef]

13. Ocampo-Perez, R.; Leyva-Ramos, R.; Alonso-Davila, P.; Rivera-Utrilla, J.; Sanchez-Polo, M. Modeling adsorption rate of pyridine onto granular activated carbon. *Chem. Eng. J.* **2010**, *165*, 133–141. [CrossRef]

14. Santos-Moreau, V.; Brunet-Errard, L.; Rolland, M. Numerical CFD simulation of a batch stirred tank reactor with stationary catalytic basket. *Chem. Eng. J.* **2012**, *207–208*, 596–606. [CrossRef]

15. Launder, B.E.; Spalding, D.B. The numerical computation of turbulent flows. *Comput. Methods Appl. Mech. Eng.* **1974**, *3*, 269–289. [CrossRef]

16. Yeoh, S.L.; Papadakis, G.; Yianneskis, M. Numerical Simulation of Turbulent Flow Characteristics in a Stirred Vessel Using the LES and RANS Approaches with the Sliding/Deforming Mesh Methodology. *Chem. Eng. Res. Des.* **2004**, *82*, 834–848. [CrossRef]

17. Yáñez-Varela, J.A.; González-Neria, I.; Alonzo-García, A.; Rivadeneyra-Romero, G.; Martínez-Delgadillo, S.A. Numerical analysis of the hydrodynamics induced by rotating ring electrode using $\kappa$-$\epsilon$ models. *Chem. Eng. Process.-Process Intensif.* **2020**, *158*, 108203. [CrossRef]

18. Al-Jabari, M. Kinetic models for adsorption on mineral particles comparison between Langmuir kinetics and mass transfer. *Environ. Technol. Innov.* **2016**, *6*, 27–37. [CrossRef]

19. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1403. [CrossRef]

20. Vivo-Vilches, J.F.; Bailón-García, E.; Pérez-Cadenas, A.F.; Carrasco-Marín, F.; Maldonado-Hódar, F.J. Tailoring the surface chemistry and porosity of activated carbons: Evidence of reorganization and mobility of oxygenated surface groups. *Carbon* **2014**, *68*, 520–530. [CrossRef]

21. Łota, G.; Krawczyk, P.; Łota, K.; Sierczyńska, A.; Kolanowski, L.; Baraniak, M.; Buchwald, T. The application of activated carbon modified by ozone treatment for energy storage. *J. Solid State Electrochem.* **2016**, *20*, 2857–2864. [CrossRef]