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Abstract: Nitrate ions are one of the causes of surface water eutrophication. In the present research, the effective adsorption of nitrate ions (NO₃⁻) on bioadsorbents prepared from yam skins (Dioscorea alata) was evaluated. The yam skin was chemically modified with ammonium chloride (NH₄Cl), and biochar was prepared from the thermally modified biomass. The results were compared with commercial coal (CC). The bioadsorbents were characterized by SEM-EDS analysis, which showed that the synthesized adsorbents have a heterogeneous surface with pores. The batch adsorption tests showed that the pH has the most significant effect on the NO₃⁻ adsorption capacity when using the modified yam skin (MYP), obtaining as best conditions pH 12 and a 0.5 mm particle size with an adsorption capacity of 25.75 mg/g; the best adsorption capacity when using the carbon synthesized from yam skin (CYP) and CC was obtained at pH 2, reaching values of 36 and 33.34 mg/g, respectively. The following performance in terms of adsorption capacity was found: CYP > CC > MYP, according to Langmuir’s model. The equilibrium isotherm of NO₃⁻ adsorption on MYP and CYP was adjusted by the Freundlich model, while the Langmuir model described adsorption on CC. The kinetics of all the systems studied showed a good fit to the pseudo-first-order, pseudo-second-order and Elovich models with R² > 0.95, suggesting a mechanism of chemical adsorption by means of species exchange between the aqueous phase and the surface of the material, with the intervention of an intraparticle diffusion stage; based on these findings, the studied biomasses reached promising adsorption capacities in the removal of nitrate anions, showing that the carbon synthesized from yam skins and modified with ammonium chloride had a remarkable behavior in comparison with commercial carbon and NH₄Cl-modified yam skins.

Keywords: adsorption; kinetics; isotherms; nitrate; yam

1. Introduction

Guaranteeing access to drinking water for the population is a vitally important issue. According to the World Health Organization (WHO), about 11% of the world’s population still does not have access to clean water, and it is expected that by 2025 half of the population will probably be living in water-scarce areas [1]. A major water pollution problem worldwide is contamination by nitrogen-containing compounds such as nitrate, nitrite and ammonium [2].

The toxicity of nitrates (NO₃⁻) in humans is attributed to reduced oxygen transport to tissues, called methemoglobinemia, which mainly affects infants under 3 months [3], and in adults it can cause stomach cancer [4]. Although nitrates are naturally present in open waters, their concentration can exceed safety thresholds due to the widespread use of nitrogen fertilizers, irrigation of crops with domestic wastewater, urban or industrial
organic waste and, above all, the use of manure and slurry derived from livestock activity as fertilizer, which cause nitrates to be released into open waters [5]. Nitrates travel rapidly in water due to their high solubility in this medium and reach the human water supply, and they are difficult to detect because they are odorless and tasteless, but are potentially toxic. The WHO established the maximum acceptable daily intake level of NO\textsubscript{3} as 0.3–0.7 mg/kg. For human water supplies, a maximum level of 50 mg/L was set as well as a quality indicator value of 25 mg/L [6]. NO\textsubscript{3}\textsuperscript{−}-contaminated water consumption is a serious global concern, especially in regions where available water sources are scarce. That is because exposure to high concentrations of nitrate can cause miscarriages, cancers (e.g., stomach, esophagus, bladder, kidney), and various ecological problems, including eutrophication, harmful algal proliferation, hypoxia/anoxia and loss of aquatic biodiversity [7].

Nitrates levels ranging from 17 to 120 mg/L have been reported in the Peddavagu region (South India) [8], 0.85–11.31 mg/L in the Yamuna River (India) [9], 1.17 mg/L in the Siriri River (Brazil) and 27.77 mg/L in the Ravi River (Pakistan) [10], showing a correlation between the number of inhabitants near water sources and the deterioration of water quality [11]. In Colombia, the Ministry of Health and Social Protection (MPS), the Ministry of Environment and Sustainable Development and the Ministry of Housing, City and Territory of Colombia regulate through Decree 1575 of 2007 [12] and Resolution 2115 of 2007 [13] the characteristics, basic instruments and frequencies of the water quality control and monitoring system with recommended levels in drinking water for human consumption. Between 2017 and 2018, values of 0.85 mg/L have been reported in samples taken at the outlet of a treatment plant in Santander [14], 0.62 mg/L at Gambote, 1.02 mg/L at Sincerín [15] and 8.46 mg/L in Matute Stream [16] in water for human consumption.

Therefore, there is a need to remove these nutrients in excess from water. A variety of common methods for removing dissolved nutrients from water and wastewater have been investigated, including biological methods, ion exchange, adsorption methods, chemical precipitation, electrocoagulation and membrane processes [17]. Adsorption has been widely explored as a nitrate removal technology and offers satisfactory results, especially with mineral-based or surface-modified adsorbents [18]. Recently, the development of high-efficiency and environmentally friendly adsorbents has become one of the main topics in the field of water treatment. Biochar has been gradually applied as a low-cost adsorbent in water treatment to successfully remove contaminants from wastewater [19,20]. That is because it is a carbon (C)-rich material formed through the thermal decomposition of biomasses, including agricultural and forestry wastes, municipal sludge, manure and other C-rich materials [21]. The characteristics of biochar that make it feasible for sorption include, among others, large specific surface area, well-developed pore structure, high C-content, large oxygen-containing functional groups, high cation exchange capacity and the presence of metallic elements in its structure [22,23].

Previous studies have examined nitrate adsorption using biochar made from various agricultural and forestry residues; when evaluating biochar prepared from rice hulls, obtained by microwave-assisted pyrolysis, a 75% nitrate removal efficiency was achieved [24]; biochar prepared with corn cob at 600 °C showed a nitrate adsorption capacity of 14.46 mg/g [25]; and by using beechwood sawdust as an adsorbent, it was found that by increasing the initial concentration from 1 to 20 mg/L, the nitrate removal capacity increases. These experiments show the effectiveness of biochar-based sorbents for the removal of nitrate in an aqueous medium. In the aqueous phase, nitrate is present in anionic form (NO\textsubscript{3}\textsuperscript{−}) due to the complete solubilization of HNO\textsubscript{3} in water. Thus, electrostatic repulsion between the nitrate and the negatively charged biochar surface is expected, which establishes one of the most critical barriers for nitrate adsorption on biochars and biomasses, showing low effectiveness when evaluated without protonating their surface [20].
In Colombia, there is a national policy oriented to the intensive cultivation of yam on the northern coast of Colombia and areas affected by the armed conflict, intending to export and satisfy national consumption; therefore, many hectares of cultivation are exploited for export and local consumption. However, large volumes of post-harvest yam remain that do not meet the quality standards for human consumption. Thus, research was motivated around industrialization, such as conversion to flour for animal feed, starch and biopolymers for food packaging, among others; therefore, this study proposes an alternative use for the large volumes of peel that will be generated in yam biorefineries as an agroindustrial rejection product, seeking to use and optimize the resources and residues from this raw material [26]. A total of 90% of yam production takes place in the departments of Bolívar, Córdoba and Sucre, on Colombia’s northern coast, with about 27,938 yam production units [26]. For this reason, the uses of yams as a source of starch production have diversified [27], including flour [28], biopolymers [29] and adsorbent materials [30,31].

Due to the high availability of residual material from yam exploitation, this work aimed to evaluate the efficacy of natural yam skins and biochar modified with NH₄Cl as adsorbent for the removal of aqueous nitrate. Morphology and surface composition of bioadsorbents were studied by scanning electronic microscopy (SEM) and X-ray dispersion spectrometry (EDS). The response surface method (RSM) was used to optimize the NO₃ adsorption capacity. Adsorption kinetic and equilibrium behavior was also studied, using mathematical models to determine adsorption mechanisms. Bioadsorption has been widely studied for the removal of cations in solution as a method of effluent treatment before discharge into the environment; however, the novelty of this study consists in modifying these bioadsorbents to test their effectiveness in the removal of anions as an alternative treatment method with low environmental impact, which seeks to reduce the environmental load of effluents discharged into the environment while solving the problem of contamination due to inadequate final disposal of agroindustrial solid waste.

2. Materials and Methods

2.1. Materials

In the present study, sodium nitrate (NaNO₃) of analytical grade, from Merck Millipore, was used for the preparation of the synthetic wastewater. The pH was adjusted with 1 M HCl and NaOH solutions. The determination of the contaminant’s remaining concentration was carried out in a Biobase UV–Vis spectrophotometer model BK-UV1900.

2.2. Methods

2.2.1. Preparation and Characterization of Adsorbents

The yam peels were collected in the best possible condition to preserve their properties. They were washed, dried at 60 °C for 5 h and reduced in a screw mill. The size classification was carried out in a shaker type sieve, Edibon Orto Alresa brand, using meshes No 35, 18 and 45 to select particles of 0.355, 0.5 and 1 mm, according to the sizes mentioned in the design of experiments [32]. The biochar was prepared using particle sizes 1 and 2 mm, to guarantee granular size [33].

The biomass was impregnated with a solution of NH₄Cl at 5% p/p, in a ratio of impregnation to precursor of 1:10, for 24 h at room temperature. It was then heat treated in a muffle up to 450 °C with a 5 °C/min ramp for 2 h. The material obtained was repeatedly washed with hot distilled water (~70 °C), until a pH close to neutral was reached in the wash water. Finally, it was dried in an oven at 110 °C until it reached a constant weight [34]. This methodology seeks to fix the modifying agent in the biochar structure by impregnating the biomass and its consequent carbonization, making NH₄Cl part of the carbon networks of the biomaterial, generating new active adsorption centers with selectivity for anionic compounds.
The SEM analysis coupled to EDS was performed using a JEOL scanning electron microscope model JSM-6490LV.

2.2.2. Adsorption Tests

For the evaluation of the adsorption capacity of yam skin modified with Nh4Cl as an adsorbent of nitrate ions present in aqueous solution, a multilevel factorial experiment design developed in Statgraphics Centurion XVI.II was followed. Particle size (0.355, 0.5 and 1 mm) and pH (2, 4, 6, 8, 10, 12) were considered independent variables and adsorption capacity as the response for a total of 18 experiments. The effect of the pH of the solution, at the selected levels, was evaluated on the adsorption capacity of the synthesized carbon and a commercial carbon, resulting in 12 experiments.

Adsorption tests were performed in an orbital shaker Lab-Shaker Incubator model IN-666, at 25 °C, shaking at 250 rpm for 24 h. For this purpose, 0.5 g of adsorbent was placed in contact with 50 mL of sodium nitrate solution with a concentration of 218 mg/L, adjusting the pH of the solutions to the values established in the design of the experiments [34]. The change in nitrate concentration was determined by UV–Vis spectroscopy at 543 nm [35]. The percentage of removal (RP) and the adsorption capacity (qe) were calculated according to Equations (1) and (2), where \( C_0 \) (mg L\(^{-1}\)) is the initial concentration, \( C_e \) (mg L\(^{-1}\)) is the final concentration, \( V \) (L) is the volume of the solution and \( w \) (g) is the mass of adsorbent [24].

\[
RP(\%) = 100 \times \left(1 - \frac{C_e}{C_0}\right)
\]

\[
q_e = \frac{(C_0 - C_e)V}{w}
\]

2.2.3. Kinetics and Adsorption Isotherms

Kinetics was studied to determine the time effect on the adsorption capacity of the evaluated bioadsorbents and the possible mechanisms involved in the adsorption process [36]. For this, 0.5 g of adsorbent was put in contact with 50 mL of synthetic NO\(_3\) solution, at 250 rpm of agitation and room temperature. Aliquots were taken at different time intervals (5, 10, 15, 20, 30, 60, 180, 360 and 540), and the experimental data of adsorption capacity were adjusted to the kinetic models [37]; pseudo-first-order by Equation (3), pseudo-second-order by Equation (4) and Elovich’s model by Equation (5), where \( q_t \) (mg g\(^{-1}\)) is the adsorption capacity at a time \( t \), \( q_e \) (mg g\(^{-1}\)) is the adsorption capacity at equilibrium, \( k_1 \) (min\(^{-1}\)) is the pseudo-first-order kinetic rate constant, \( t \) (min) is time, \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the pseudo-second-order rate constant, \( \alpha \) (mg g\(^{-1}\) min\(^{-1}\)) is the constant of the Elovich equation and \( \beta \) (g mg\(^{-1}\)) is the exponent in the Elovich equation.

\[
q_t = q_e (1 + e^{-kt})
\]

\[
q_t = \frac{t}{k_2q_e^2 + q_e}
\]

\[
q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t)
\]

Adsorption isotherms were performed to describe the amount of NO\(_3\) adsorbed at the equilibrium [38]; the tests were performed at different initial contaminant concentrations (50, 80, 134 and 218 mg/L) for 24 h. The experimental data were adjusted to the models of Langmuir (Equation (6)), Freundlich (Equation (7)), and Dubinin–Radushkevich (Equation (8)); where \( q_{\text{max}} \) (mg g\(^{-1}\)) is the maximum adsorption capaci-
ty, b (L mg⁻¹) is Langmuir’s constant related to the heat of adsorption, \( C_e \) (mg L⁻¹) is the residual concentration of solute in solution, \( q_e \) (mg g⁻¹) is the amount of adsorbate retained by the adsorbent in equilibrium, \( K_F \) (mg g⁻¹ (L mg⁻¹)\(^n\)) and \( n \) are the Freundlich rate constants referring to adsorption capacity and adsorption intensity, respectively, \( q_{DR} \) (mg g⁻¹) is the adsorption capacity of the Dubinin–Radushkevich model, \( K_{DR} \) (mol² kJ⁻²) is the Dubinin–Radushkevich rate constant related to adsorption energy, \( E \) (kJ mol⁻¹) is the average adsorption energy per molecule of adsorbate required to transfer one mole of the ion from the solution to the adsorbent surface and \( \varepsilon \) is the Polanyi potential which is temperature dependent.

\[
q_e = \frac{q_{\text{max}} b C_e}{1 + b C_e} 
\tag{6}
\]

\[
q_e = K_F C_e^{1/n} 
\tag{7}
\]

\[
q_e = q_{\text{DR}} e^{-K_{\text{DR}} \varepsilon^2} 
\tag{8}
\]

\[
E = \frac{1}{\sqrt{2K_{\text{DR}}}} \quad \varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) 
\tag{9}
\]

\[
E = \frac{1}{\sqrt{2K_{\text{DR}}}} \quad \varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) 
\tag{10}
\]

The non-linear adjustment of the mathematical models was carried out in OriginPro 8® software.

3. Results and Discussion

3.1. Bioadsorbent Characterization

According to the SEM micrograph, YP exhibits an irregular surface and mesopores (Figure 1a) [39]. It was evidenced that carbon, calcium and oxygen are present in both materials, with YP being the one with the most diverse structure, with traces of multiple elements such as potassium, silicon, aluminum, phosphorus, iron and copper [40]. These elements are related to the functional groups present in lignocellulosic materials [41] and their ability to capture contaminants due to electrostatic forces. They also presented agglomerates of particles from pectin, cellulose, lignin and wax [42]. After the NO₃ adsorption, a porous surface in the form of a mesh and the appearance of folds in the bio-material are observed (Figure 1b) [43]. There is evidence of the appearance of nitrogen in the high-intensity peak of 0.065 keV, which indicates that removal of the anion was successful [41]. The disappearance of Cu, P and S is also observed, and the decreasing in weight % of O, Al, Ca, Fe, Si and K.
Biochar synthesized from yam skins and modified with NH₄Cl exhibited a heterogeneous surface with folds and pores (Figure 2a). The pores are in the macro- and mesopore range and allow access to the microporous structure. The presence of agglutinated networks in the exposed area is shown, which is attributed to the degree of aromaticity; the order of the graphitized structure was affected by the volatilization of the oxygen and hydrogen present in the YP structure, thus forming new aromatic bonds [44]. The morphology of the bioadsorbent was agglutinated after removing the anion, with the disappearance of the folds and the nets; likewise, it is observed that the surface is smoother. As with the MYP (Figure 1b), the EDS after adsorption showed the presence of nitrogen in the spectrum (Figure 2b), suggesting that the removal of the anion was successful [41].
Figure 2. SEM micrographs and EDS spectrum of biochar (a) before and (b) after NO$_3^-$ adsorption.

Figure 3 shows the interactions between the bioadsorbents impregnated with NH$_4$Cl and the NO$_3^-$ anion. The charge of the bioadsorbent surface groups enhances the electrostatic interactions with the contaminant. It allows the capture of the nitrogen nutrient, which is evidenced in Figures 1b and 2b, with a strong N peak in the EDS. Previously, Fotsing et al. [42] found that the adsorption of nitrate on coconut shell functionalized with 3-aminopropyltriethoxysilane occurs through different steps, namely: coating of the adsorbent, diffusion of the contaminant to the outer surface of the adsorbent, diffusion at the effective internal adsorption site and capture of the contaminant on the surface of the modified adsorbent. Considering that the adsorption process involves physisorption and chemisorption on the bioadsorbents under study, it can be postulated that adsorption takes place by protonation of the active centers due to the introduction of NH$_3^+$ groups during the impregnation of the yam peels and the surface becomes positively charged, thus favoring the adsorption of nitrate [45].

Figure 3. Scheme of interactions between NO$_3^-$ and biochar adsorbent.

3.2. Adsorption Tests

From the adsorption tests using MYP, it was found that the increase in NO$_3^-$ adsorption capacity is proportional to the increase in the initial pH of the solution (Figure 4); from pH 4 on, the effect of this variable is not very significant in the process, suggesting that the number of positive surface charges remains the same. From pH 8, the concentration of OH ions increases and, therefore, competition from OH for the adsorption of nitrates may arise, then nitrates are adsorbed less [46]. However, the higher removal rate of NO$_3^-$ at pH 12 could be due to its conversion to the gaseous species NH$_3$ and NH$_4^+$, which
can volatilize during the removal process or be retained in the active centers of the adsorbent [47]. H+ ions would strongly compete against the cationic species at lower pHs for active adsorption sites on the biochar surface, thus inhibiting adsorption capacity and removal efficiency. In addition, the protonation of negatively charged functional groups on the biochar surface hinders the interaction between the species and the biochar surface [48]. The highest adsorption capacity was obtained at 0.5 mm, which is due to the fact that a small particle has a larger surface area thanks to the number of pores per unit of mass, which favors the number of active binding sites and the available contact surface, resulting in a higher mass transfer and fast adsorption [49]. The highest adsorption capacity of the anion under study was obtained at pH 12 and 0.5 mm of particle size.

![Graph showing adsorption capacity vs pH and particle size](image)

**Figure 4.** Effect of pH and particle size on the adsorption capacity of NO₃ on MYP.

Table 1 shows the results obtained from the analysis of variance with a confidence level of 95%, finding that pH is the significantly influential effect on nitrate adsorption capacity on MYB, with an absolute error of 2.86.

| Source     | Sum of Squares | F-Ratio | p-Value |
|------------|----------------|---------|---------|
| A: pH      | 128.0          | 7.36    | 0.0188  |
| B: Particle size | 28.6  | 1.64    | 0.2243  |
| AA         | 0.959          | 0.05    | 0.8186  |
| AB         | 1.54           | 0.09    | 0.7712  |
| BB         | 2.13           | 0.12    | 0.7328  |
| Total error| 209.0          |         |         |
| Total (corr.) | 371.0 |         |         |

Likewise, from the application of the RMS, the second-order equation describing the adsorption process was obtained, revealing that the regression is statistically significant, and based on the ANOVA results, the regression model of Equation (11) reports a high R² value of 96.23%, which implies a high correlation between the observed values and predicted values [50].

\[
q_e = 20.5 + 0.679A - 12B + 0.023A^2 - 0.326AB + 7.02B^2
\] (11)
where $q_t$ (m/g) is the adsorption capacity of the adsorbent, $A$ is the pH of the solution and $B$ (mm) is the adsorbent particle size. The positive and negative signs before the terms indicate the synergistic and antagonistic effect of the respective variables [51,52].

When using carbon from yam skins (CYP) and commercial carbon, it is observed that the increase in pH has an inversely proportional effect on the increase in adsorption capacity. The adsorption capacity is observed to reach its maximum at pH 2 and decreases with increasing pH (Figure 5). This could be due to the fact that, when the pH of the solution increases, the surface of the adsorbents is negatively charged and the adsorption capacity of nitrate decreases, because the negatively charged surface sites on the adsorbent did not favor nitrate due to electrostatic repulsion [53,54].

The behavior shown by CYP and CC was similar to that reported when clay was used in the removal of nitrate, obtaining the highest adsorption capacity of 3.25 mg/L at pH 2 [54]. The same trend was observed when using biochar prepared from quaternized sugar cane bagasse, achieving an adsorption capacity of 28.3 mg/g at pH 2 [55]. It is clear that as the pH increases, the adsorption of nitrate decreases. This is due to increased competition between nitrate and hydroxide ions for the same sites on the adsorbent surface. Additionally, at acidic pH, the surface of the bioadsorbent is positively charged thanks to protonation, which increases the electrostatic attraction between the sorbate surface and the negatively charged nitrate ions.

![Figure 5. pH effect on NO₃ adsorption capacity on CYP and CC.](image)

Table 2 shows that when evaluating CYP and CC, the most influential parameter is pH with an absolute error of 1.85; it was found that the decrease in this factor favors the adsorption capacity of nitrate on the evaluated carbons due to the protonation of the active centers located on the surface of the adsorbent, which allows the anion to be electrostatically attracted to the active sites and captured there (Figure 3).

Table 2. Analysis of variance for NO₃ adsorption on CYP and CC.

| Source       | Sum of Squares | F-Ratio | $p$-Value |
|--------------|----------------|---------|-----------|
| A: Adsorbent type | 31.9           | 4.11    | 0.0821    |
| B: pH        | 253.0          | 32.55   | 0.0007    |
| AB           | 15.7           | 2.03    | 0.1975    |
| BB           | 0.0199         | 0.00    | 0.9610    |
| Total error  | 54.3           |         |           |
| Total (corr.)| 355.0          |         |           |
| A: Adsorbent type | 31.9           |         |           |
From the application of the RMS, the second-order equation describing the adsorption process was obtained, revealing that the regression is statistically significant, and based on the ANOVA results, the regression model in Equation (12) reports a high $R^2$ value of 94.7%, which implies a high correlation between the observed values and predicted values [50].

$$q_t = 38.7 - 1.43A - 2.41B + 0.671AB + 0.0041B^2$$  \hspace{1cm} (12)

where $q_t$ (mg/g) is the adsorption capacity of the adsorbent, $C$ (mg/L) is the initial concentration of the contaminant, $T$ (°C) is the temperature and $D$ (g) is the adsorbent dose. The positive and negative signs before the terms indicate the synergistic and antagonistic effect of the respective variables [51,52].

3.3. Adsorption Equilibrium

Adsorption equilibrium was performed by studying the isotherms at room temperature, 250 rpm agitation, 0.5 g of adsorbent dose, at initial concentrations of 50, 80, 134 and 268 mg/L. The experimental data were adjusted to Langmuir, Freundlich and Dubinin–Radushkevich models by non-linear regression using Origin Pro 8® software. The best fit was chosen according to the correlation coefficient $R^2$ (Table 3) [20].

### Table 3. NO$_3$ adsorption isotherm setting parameters.

| Model                  | Parameters   | MYP          | CYP          | CC            |
|------------------------|--------------|--------------|--------------|---------------|
| Langmuir               | $K_L$ (L/mg) | $3.698 \times 10^{-5}$ | 0.0163 | 0.019 |
|                        | $q_{max}$ (mg/g) | 7.675 | 10.834 | 8.612 |
|                        | $R^2$        | 0.773 | 0.971 | 0.996 |
| Freundlich             | $K_F$ (L/g)  | 1.012 | 0.696 | 0.738 |
|                        | $n$          | 0.615 | 2.058 | 2.304 |
|                        | $R^2$        | 0.955 | 0.991 | 0.966 |
| Dubinin–Radushkevich   | $K_{DR}$ (mol$^2$/kJ$^2$) | $3.275 \times 10^{-6}$ | 5.789 | 7.266 $\times 10^{-5}$ |
|                        | $q_{DR}$ (mg/g) | 33.999 | 6.747 | 5.975 |
|                        | $E$ (KJ/mol)  | 390.737 | 92.936 | 82.954 |
|                        | $R^2$        | 0.875 | 0.629 | 0.808 |

It was found that the $q_{max}$ of the adsorbents presented the pattern CYP > CC > MYP, showing that the surface modification of the biocarbon increases the adsorption capacity of the biomaterial, and promotes the creation of NO$_3$-related active sorption centers, in order to obtain a comparative basis, Table 4 shows the values of $q_{max}$ for different adsorbents. The isotherm of NO$_3$ adsorption on MYP and CYP was adjusted by Freundlich’s model, indicating that the process was multilayered through the pores of the adsorbent, due to the different activation energies of the active centers [24]. Freundlich’s $n$ parameter is >1 for CYP, which suggests that the affinity of the sorption sites for the contaminant is high, so the process would be favorable [56]. Langmuir’s model described the isothermal adsorption on commercial coal, which indicates that the process occurred through the formation of a monolayer on the surface of the adsorbent with a homogeneous affinity for the active centers [57].

It is observed that the results obtained in the present study for the removal of NO$_3$-are in the lower extreme of the range reported, from 5 mg/g to 232.56 mg/g, with those reported in the present study being superior to those found when using chitosan doped with Fe$^{3+}$ nanoparticles [58] and zeolite modified with cetylpyridinium bromide. It is evidenced that the most effective modifications involve the quaternization of bioadsorbents with epichlorohydrin, pyridine and quaternary salts such as N,N-dimethylformamide, trimethylamine and diethylenamide.
### Table 4. $q_{\text{max}}$ values using different adsorbents.

| Adsorbent                                                                 | $q_{\text{max}}$ (mg/g) | Reference |
|---------------------------------------------------------------------------|--------------------------|-----------|
| Functionalized cellulose grafted epichlorohydrin                          | 232.56                   | [59]      |
| Anionic biographene nanosheet                                              | 182.506                  | [60]      |
| Cheat straw crosslinked with epichlorohydrin and dimethylamine            | 128.97                   | [61]      |
| Crosslinked chitosan beads                                                | 104.0                    | [62]      |
| Magnetic amine-crosslinked biopolymer based on corn stalk                 | 102.04                   | [63]      |
| Rice hull                                                                 | 74.41                    |           |
| Amberlite IRA-900                                                         | 74.41                    | [64]      |
| Pine bark                                                                 | 65.73                    |           |
| Moringa husk                                                              | 63.25                    |           |
| Sugarcane bagasse                                                         | 63.25                    |           |
| Coconut shell                                                             | 55.18                    | [64]      |
| Wheat stalk resin                                                          | 50.24                    | [65]      |
| Persimmon tealeaf                                                         | 48.36                    | [64]      |
| Lauan sawdust                                                             | 47.74                    |           |
| *Arundo donax* L. reed-based anion exchange resin                          | 44.61                    | [66]      |
| Cotton stalk resin                                                        | 39.15                    | [65]      |
| Chitosan microspheres                                                     | 32.15                    | [4]       |
| Polyurethane/sepiolite cellular nanocomposites                            | 23.30                    | [3]       |
| Carbon from yam peel modified with NH4Cl                                  | 10.834                   | Present study |
| Activated carbon modified with cetyl trimethyl ammonium chloride          | 10.80                    | [67]      |
| Granular Fe–Zr–chitosan complex                                           | 10.60                    | [68]      |
| Zeolite modified with cetylpyridinium bromide                              | 9.68                     | [69]      |
| Commercial carbon                                                         | 8.612                    | Present study |
| Organosilica                                                              | 7.75                     | [70]      |
| Yam peel modified with NH4Cl                                               | 7.675                    | Present study |
| Chitosan doped with Fe$^{3+}$                                              | 5.00                     | [58]      |

#### 3.4. Adsorption kinetics

Kinetics was evaluated to analyze the effect of time on the adsorption process and determine the adsorbent’s service time. Elovich’s models, pseudo-first and pseudo-second order, were used to adjust the experimental data and identify the possible mechanisms involved in the adsorption [39]. The adsorption kinetics are presented in Figure 6, and the parameters of adjustment to the models are summarized in Table 5.

### Table 5. NO3 adsorption kinetics parameters.

| Model                      | Parameter | MYP     | CYP     | CC       |
|----------------------------|-----------|---------|---------|----------|
| Pseudo-first order         | $q_e$ (mg/g) | 21.389  | 26.669  | 24.621   |
|                            | $k_1$ (min$^{-1}$) | 26.955  | 1.175   | 1.357    |
|                            | R$^2$     | 0.984   | 0.999   | 0.999    |
| Pseudo-second order        | $q_e$ (mg/g) | 21.389  | 24.701  | 24.636   |
|                            | $k_2$ (g/mg*min) | $1.483 \times 10^{16}$ | 1.329   | 2.957    |
|                            | R$^2$     | 0.984   | 0.999   | 0.999    |
| Elovich                    | $\alpha$ (mg/g*min) | 5.005   | 4.403   | 4.400    |
|                            | $\beta$ (g/mg) | $1.242 \times 10^{14}$ | $7.015 \times 10^{14}$ | $5.374 \times 10^{14}$ |
|                            | R$^2$     | 0.971   | 0.998   | 0.998    |
Figure 6. Adjustment of NO₃ adsorption kinetics over (a) MYP, (b) CYP and (c) CC.

It is observed that rapid adsorption occurs in the first minutes of the process, due to the availability of active sites, and that equilibrium is reached in the first 30 min in all cases. The fast adsorption in the initial minutes of the process is due to the influence of diffusive phenomena from the solution to the surface of the adsorbent and later to the interior of the pores [5]. In the kinetics of nitrate adsorption on MYP, a decrease in the amount of adsorbed solute is observed due to the biomass’s surface saturation by NO₃ ions [60]. In a prior study, a similar behavior to that found when using MYP was observed when using commercial Cloisite® 10A; the reduction in the number of adsorbent anions over time did not have a clear explanation [70] as well as when using an organoclay prepared using montmorillonite and hexadecylpyridinium chloride [71] and onion peels [72]. This suggests that during the adsorption process, desorption episodes occur, especially when the time is prolonged. In addition, this would provide valuable information for the determination of the service life of the adsorbent. The adsorption of NO₃ on the evaluated adsorbents was adjusted to the three tested models, with $R^2 > 0.95$ in all cases. This suggests that the speed-limiting step of adsorption is chemisorption due to physicochemical interactions between the two phases [73], and the rate of adsorption depends on a mechanism operating at active sites on the surface of the biomass [39]. Although the kinetic constants of the MYP were the highest, it was the adsorbent that presented less adsorption capacity, obtaining $q_e$ of the order CYP > CC > MYP.

4. Conclusions

The present investigation concluded that: (i) evaluated biosorbents are potentially good for use in NO₃ adsorption, obtaining the following performance in terms of adsorption capacity: CYP > CC > MYP. (ii) The SEM-EDS analysis showed that the adsorbents have a heterogeneous surface with pores, and the adsorption process is given by the interaction between the anion and cationic adsorption sites in the structure of the bioadsorbents. (iii) It was found that the pH has the most significant effect on the adsorption capacity of NO₃ when using MYP, obtaining as best conditions pH 12 and 0.5 mm of particle size, achieving an adsorption capacity of 25.75 mg/g; when using CYP and CC, the best adsorption capacity was observed at pH 2 with values at 36 and 33.34 mg/g, respectively. (iv) The isotherm of NO₃ adsorption on MYP and CYP was adjusted by Freundlich’s model, which indicates that the process occurred in multilayers through the pores of the adsorbent, while the equilibrium over CC adsorption was adjusted to Langmuir’s model, indicating that the process occurred by means of the formation of a monolayer on the surface of the adsorbent. (v) The adsorption kinetics of NO₃ was fast in the initial minutes, achieving equilibrium in the first 30 min for all the evaluated adsorbents, with good adjustment to the pseudo-first-order, pseudo-second-order and Elovich models with an $R^2 > 0.95$, suggesting that the adsorption mechanism is chemisorption by means of the exchange of species between the aqueous phase and the surface of the material, with the intervention of an intraparticle diffusion stage.

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