Phosphate removal from water using activated carbon derived from *Ampelodesmos mauritanicus* stems: equilibrium and kinetic studies

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**A B S T R A C T**

This paper describes the synthesis and characterization of *Ampelodesmos mauritanicus* stem-derived activated carbon (AMSAC). The activated carbon was produced by phosphoric acid activation followed by carbonisation and was characterized by N$_2$ adsorption–desorption isotherm, scanning electron microscopy, energy-dispersive X-ray analysis, and Fourier-transform infrared (FTIR) spectroscopy. The sorption potential of AMSAC for the removal of phosphate ions from the water was investigated. The effects of contact time, initial pH, and initial phosphate concentration on the sorption process were studied. The optimum contact time and pH for removal of phosphate ions was 75 min and pH 6–7. The experimental data showed that AMSAC had a high Brunauer–Emmett–Teller surface area of 1,293 m$^2$/g and abundant pores with a specific volume of 1.23 m$^3$/g. FTIR analysis revealed various functional groups on the surface of the AMSAC, which can play an important role in the adsorption process. A Langmuir isotherm model fits the equilibrium data for the sorbent well compared to the Freundlich, Temkin, and Dubinin–Radushkevich isotherm models. The monolayer sorption capacity of AMSAC for PO$_4^{3-}$ ions was determined to be 4.52 mg/g at 25°C. The experimental data were also modelled using the sorption kinetic models. It was found that the kinetic data were described better by the pseudo-second-order adsorption kinetic model. Therefore, AMSAC is a promising low-cost phosphate sorbent that can be produced from plentiful and annually renewable plants.

**Keywords:** Phosphoric acid; Adsorption isotherm; Phosphate; Characterisation; *Ampelodesmos mauritanicus*

1. Introduction

Phosphate discharged into water bodies such as lakes, ponds, and rivers are not considered toxic, but is responsible for eutrophication, which causes oxygen depletion, toxic algae blooms, and degradation of water quality [1,2]. Phosphate comes to water resources from agricultural fertilizers, detergents, erosion of soils, and discharge from sewage treatment plants and often presents in water and wastewater at various concentrations. The principal phosphorus compounds in wastewater are generally orthophosphates together with smaller amounts of organic phosphate [3]. Studies indicate that 10–15 mg/L phosphate may be contained in municipal wastewater, whereas effluent from chemical industries, such as detergent manufacturing and metal coating processes, may contain 14–25 mg/L phosphate [4,5]. Protection of water resources is an urgent task for healthy living and sustainable development. In many countries, stringent regulations limit phosphorus levels to 0.05 mg/L to maintain an ecologically sustainable status [6]. For water conservation, the removal of phosphates from waters and wastewaters to control eutrophication is of great importance. Phosphate removal from wastewater has been widely investigated, and several techniques have

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been developed, including physical processes (settling, filtration), chemical precipitation (with aluminium, iron, and calcium salts), and biological processes that rely on biomass growth (bacteria, algae, and plants) or intracellular bacterial polyphosphate accumulation [7–9]. The sorption process is generally considered to be an effective water treatment option to remove anions because of convenience, ease of operation, and simplicity of design and economics, provided that low-cost sorbents are used [10]. Recently, the adsorption of phosphate onto activated carbon derived from plant materials has received increasing attention, as activated carbon could be a low-cost and effective adsorbent for phosphate removal in water and wastewater [11,12].

The activated carbon that was investigated in this study was produced from the stems of the Ampelodesmos mauritanicus plant, which is a grass plant of the family Gramineae largely present in the Mediterranean area and, in particular, North Africa. It grows both in wet and dry areas and is abundantly available throughout the year, which makes it important biomass. The average height of the A. mauritanicus plant can exceed one meter, and their fibres are extremely sturdy and tough [13–15]. The main constituents of A. mauritanicus according to their weight proportions are cellulose (44.1%), hemicelluloses (27%), lignin (16.80%), extractives (9%), and ashes (3.1%) [16].

The aim of this work is to prepare activated carbon powder from A. mauritanicus stems using chemical activation with H₃PO₄ followed by carbonization in nitrogen atmosphere. Characterisation of the activated carbon obtained in the optimal conditions was conducted using the following techniques: Fourier-transform infrared (FT-IR) spectroscopy to determine the functional groups, Brunauer–Emmett–Teller (BET) method to determine surface area and average pore size, scanning electron microscopy (SEM) to investigate the structure and morphology, and iodine and methylene blue number. The potential of the prepared AMSAC is evaluated for phosphate removal from plant materials has received increasing attention, as activated carbon could be a low-cost and effective adsorbent for phosphate removal in water and wastewater [11,12].

2. Experimental

2.1. Sample preparation

2.1.1. Raw material

A. mauritanicus (Fig. 1) was collected from the northeast of the Boumerdes area, Algeria. This biomass material was harvested in early June 2016. The sample was washed with water to remove dirt, dried at 60°C for 8 h in an air oven, and reduced to about 2 cm in length with a razor blade for effective milling to a size less than 500 µm. The residues after this milling were used for the compositional analysis and production of AMSAC.

2.1.2. Adsorbent synthesis

A. mauritanicus trunk powder was thoroughly mixed with ortho-phosphoric acid H₃PO₄ solutions (85%) in a weight ratio of 1:2 g/g (ortho-phosphoric acid was purchased from Merck Germany) at room temperature for 1 h and then dried in an oven (Memmert UNB 400) at 105°C for 24 h. After the impregnation step, the sample was carbonized in a horizontal tube furnace (Nabertherm, Germany) under nitrogen atmosphere. The heating rate and the nitrogen flow rate were 5°C/min and 200 mL/min, respectively. The samples were kept at 500°C for 2 h. The crucibles were left inside the furnace for 24 h to cool down at room temperature. The prepared AMSAC samples were soaked in 0.1 N NaOH for 2 h, as the pH of the washing water reached about 5, and then with 2 L of hot de-ionized water under reflux until the pH of the rinsing water was neutral. The samples were filtered through a Whatman filter paper (0.45 µm) to separate the supernatant and the AMSAC particles. After that, it was dried in a hot air oven for 24 h, weighed, and packed in sealable plastic bags for further use.

2.1.3. Adsorbate

The 500 mg/L phosphate (PO₄³⁻) stock solution was prepared by dissolving potassium dihydrogen orthophosphate (KH₂PO₄) powders (analytical reagent grade) in deionized water. Phosphate working solutions with different concentrations were prepared by diluting the PO₄³⁻ stock solution with distilled water and using 0.01 M KCl to adjust ionic strength. The pH value of the PO₄³⁻ working solution was adjusted with diluted HCl and NaOH before the adsorption experiments.

2.1.4. Adsorbent characterisation

The surface structure of AMSAC was investigated with a SEM, N₂ adsorption–desorption technique (BET method), FTIR, and X-ray diffraction (XRD). A SEM was used to characterize the nanoparticle shape and size using an FEI Quanta 650 scanner with an accelerating current of 80 µA and a voltage of 30 kV. SEM images were formed using transmitted electrons (instead of the visible light), which can produce magnifications up to 100,000 X with resolutions up to 100 Å. The BET surface area was measured by the N₂ adsorption–desorption technique using a Quanta Chrome Instruments Nova 2000 E analyzer. The total pore volume was defined as the volume of liquid
nitrogen corresponding to the amount adsorbed at a relative pressure of \( P/P_r = 0.99 \). The mesoporous surface area and microporous volume were estimated using a t-plot [17]. The FTIR spectroscopy of the AMSAC was measured by an FTIR spectrometer Shimadzu 8400S from 4,000 to 400 cm\(^{-1}\). The measurement was carried out with the KBr pellet method (0.5% of the sample in KBr). The crystalline structure was analyzed by the XRD using Cu-K\(\alpha\) radiation (1.5418 Å) of a Bruker D8 Advance diffractometer operating at 40 kV, 40 mA for angles between \( 2\theta = 4°-90° \) in 0.02° steps. The bulk density was determined according to a procedure followed by Toshiguki and Yukata [18]. Moisture content was determined using an oven drying method [19]. Ash content was determined by a standard method [20]. The adsorption properties of the activated carbons where characterized in terms of both iodine adsorption and methylene blue adsorption indexes according to the procedure reported in the literature [21,22]. The phosphate content in the filtrates and initial solutions was measured by the molybdate blue complex spectrophotometric method at \( \lambda_{\text{max}} \) of 880 nm using a Lambda 25 UV/VIS spectrophotometer (Perkin-Elmer, Germany). This experiment was performed in triplicate and average values were reported.

2.3. Batch adsorption studies

2.3.1. Removal efficiency and adsorption capacity

The removal of phosphate ions from the aqueous synthetic solution was conducted using batch experiments, including isotherm studies, kinetic studies, and initial pH studies. All the experiments were conducted in batch mode by adding 50 mL of phosphate solution to 0.1 g of AMSAC (initial solution concentration ranging from 5 to 60 mg/L, temperature at 25°C ± 1°C, and pH = 6.8) in 250 mL Erlenmeyer flasks. The flasks were shaken using a horizontal shaker (Edmund Buhler 7400 Tubingen, SM 25, Germany) operating at 200 rpm for 50 min. After the shaking of the slurries, the suspensions were centrifuged using a centrifuge apparatus (HERAEUS MULTIFUGE 3RS, Kendro GmbH, Germany) operating at 3,000 rpm for 10 min and immediately filtered using a vacuum filtration pump employing a 0.45 µm filter to obtain a clear supernatant aliquot. The supernatant solution obtained from filtration was used for the phosphate analysis. The adsorbed and % removal of phosphate was computed using Eqs. (1) and (2), as indicated below:

\[
q_t = \frac{(C_0 - C_t) V}{M} \quad (1)
\]

\[
(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)
\]

where \( q_t \) is the amount of phosphate adsorbed per unit mass of adsorbent (mg/g) at time \( t \), \( C_0 \) and \( C_t \) are the initial and final concentration of phosphate at time \( t \) (mg/L), respectively, \( V \) is the volume of the solution contacted with the adsorbent (L), \( M \) is the mass of the adsorbent (g), and (\%) is the percent removal at the time (t).

2.3.2. Effects of initial pH

For the initial pH studies, it was adjusted to be in the interval 2.0–14 with 0.1 N HCl or 0.1 N NaOH solutions using a pH meter (HANNA instruments pH 213). Experiments were conducted at an initial phosphate ion concentration of 40 mg/L, an adsorbent dose of 4 g/L, room temperature (25°C ± 1°C), and a spin time of 50 min.

2.3.3. Kinetic studies

For the kinetic study, AMSAC (0.2 g) was agitated for a selected time interval of 5, 10, 15, 30, 40, 80, 120, 160, and 200 min at 200 rpm in a series of 250 mL conical flasks containing 50 mL of aqueous solution (40 mg/L) of PO\(_4^{3-}\) and distilled water maintained at 25°C ± 1°C in the horizontal shaker. Each time interval was repeated three times to find the deviation in the measured value. In this work, the kinetic data were analyzed using the pseudo-first-order, pseudo-second-order, Elovich, and intra-particle-diffusion kinetic models with a calculation of the nonlinear chi-square test (Eq. (3)) of the adsorption capacity from each model. All the models used were linearized, and the model with a linearity closest to 1 with a lower percentage of variance was considered as the best model to explain the mechanism.

\[
\chi^2 = \sum \frac{(q_{\text{cal}} - q_{\text{exp}})^2}{q_{\text{max}}} \quad (3)
\]

where \( q_{\text{max}} \) and \( q_{\text{cal}} \) are the maximum and calculated amount of phosphate adsorbed (mg/g), respectively.

The equation for the pseudo-first-order kinetic model can be expressed by Eq. (4):

\[
\log(q_e - q_t) = \log(q_e) - K_1 \frac{t}{2.303} \quad (4)
\]

where \( K_1 \) is the rate constant of the pseudo-first-order model of adsorption (min\(^{-1}\)), and \( q_e \) and \( q_t \) are the amount of phosphate adsorbed (mg/g) at equilibrium and at time (t), respectively.

The values of \( K_1 \) and \( q_e \) can be obtained from the slope and the intercept of a linear straight-line plot of \( \log(q_e - q_t) vs. t \).

The equation for the pseudo-second-order kinetic model can be written as shown in Eq. (5):

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \quad (5)
\]

where \( K_2 \) is the rate constant of the pseudo-second-order model of adsorption (g/mg min). The value of \( K_2 \) and \( q_e \) can be obtained from the slope and intercept of a plot of \( t/q_t \) vs. \( t \) (min).

The Elovich equation was used to interpret the kinetics of sorption that was previously described as chemical sorption on highly heterogeneous sorbents. The equation had been simplified and linearized as shown in Eq. (6):
\[ q_t = \frac{1}{\beta} \ln t + \frac{1}{\beta} \ln (\alpha \beta) \]  

(6)

where \( \alpha \) is the initial adsorption rate (mg/(g min)) and \( \beta \) is the desorption rate (mg/g).

The intra-particle diffusion was explored using a linear intra-particle diffusion kinetic model, which can be expressed by Eq. (7):

\[ q_t = K_p t^{1/2} + C \]  

(7)

where \( K_p \) is the intra-particle diffusion rate constant (mg/(g min^{1/2}) and \( C \) is a constant related to the thickness of the boundary layer (mg/g).

If the plot of \( q_t \) vs. \( t^{1/2} \) gives a straight line, the sorption process is controlled by intra-particle diffusion only.

### 2.3.4. Adsorption isotherm models

#### 2.3.4.1. Langmuir isotherm

The Langmuir isotherm is most widely used for the sorption of a pollutant from a liquid solution. The model assumes that the sorption takes place at specific homogeneous sites within the adsorbent. The Langmuir equation is represented as follows:

\[ q_e = \frac{q_0 K_e C_e}{1 + K_e C_e} \]  

(8)

where \( q_e \) is the mass of phosphate ions adsorbed on the adsorbent at equilibrium (mg/g), \( C_e \) is the equilibrium concentration of phosphate ions (mg/L), \( q_0 \) is the maximum adsorption capacity (mg/g), and \( K_e \) is a Langmuir constant (L/mg) related to the energy of adsorption.

The linear form of the Langmuir isotherm is:

\[ \frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{K_e q_0} \]  

(9)

The essential characteristic of the Langmuir isotherm may be expressed in terms of a dimensionless separation parameter \( R_L \), which is indicative of the isotherm shape that predicts whether an adsorption system is unfavourable (\( R_L > 1 \)), linear (\( R_L = 1 \)), or favourable (\( 0 < R_L \)). \( R_L \) is defined as:

\[ R_L = \frac{1}{1 + (1 + K_e / C_e)} \]  

(10)

where \( C_e \) is the initial concentration (mg/L).

#### 2.3.4.2. Freundlich isotherm

The Freundlich isotherm is an empirical equation to describe heterogeneous adsorption systems. This isotherm is given as:

\[ q_e = K_f C_e^n \]  

(11)

where \( K_f \) is the Freundlich constant (L/g) related to the bonding energy and \( 1/n \) is the heterogeneity factor in which \( n \) is a measure of the deviation from linearity of the adsorption. A linear form of the Freundlich expression is:

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  

(12)

#### 2.3.4.3. Temkin isotherm

The Temkin isotherm has been used in the following form:

\[ q_e = \frac{RT}{b} \ln (K_T C_e) \]  

(13)

where \( RT/b = B \), \( R \) is the gas constant (8.31 J/Mol K), \( T \) is the absolute temperature, \( K_T \) is the Temkin isotherm equilibrium binding constant (L/g), and \( b \) is the Temkin isotherm constant.

A linear form of the Temkin isotherm can be expressed as:

\[ q_e = \frac{RT}{b} \ln (K_T) + \frac{RT}{b} \ln (C_e) \]  

(14)

#### 2.3.4.4. Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich isotherm assumes that there is a surface area where the adsorption energy is homogeneous. The Dubinin–Radushkevich equation has the following form:

\[ q_e = q_{\text{max}} \exp (-\epsilon / \varepsilon) \]  

(15)

where \( q_{\text{max}} \) is the Dubinin–Radushkevich monolayer capacity (mg/g), \( K_r \) is the constant related to the mean free energy (E) of adsorption per mole of the adsorbate (mol^2/kJ^2), which can be computed using the relationship:

\[ E = (2k)^{-1/2} \]  

(16)

and \( \varepsilon \) is the Polanyi potential, which is related to the equilibrium concentration as follows:

\[ \varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \]  

(17)

A linear form of the Dubinin–Radushkevich isotherm is:

\[ \ln q_e = \ln q_{\text{max}} - K_r \varepsilon^2 \]  

(18)

In this analysis, the correlation coefficient \( (r^2) \) and nonlinear chi-square test \( (\chi^2) \) were used to determine the best-fitting
isotherm with the experimental data. The mathematical derivation is given by Eq. (19).

\[
\chi^2 = \sum \left( \frac{q_e - q_{e,\text{cal}}}{q_e} \right)^2
\]  

(19)

where \( q_{e,\text{cal}} \) is the equilibrium capacity (mg/g) calculated from the model.

\( \chi^2 \) will be a small number when the data from the model are similar to the experimental data.

3. Results and discussion

3.1. Characterisation of A. mauritanicus stem-derived activated carbon

The AMSAC prepared under the condition mentioned above was produced with a final yield of 37.54 wt.%, which is a similar value to those reported previously by other authors [23–25]. In view of the data in Table 1, AMSAC shows a high moisture content (9.63%), low percentage of volatile matter (30.5%), average bulk density (0.255 g/mL), high fixed carbon content (54.15%), and low ash content (6.72%). Furthermore, the impregnation of stems with H\(_3\)PO\(_4\) followed by a thermal treatment under nitrogen gas creates cavities on the surface of the activated carbon and increases its porosity and specific surface area due to the evaporation of activating agents during carbonization [26,27]. The BET surface area results indicate that AMSAC has a surface area of 1,293 m\(^2\)/g. This value is higher than that reported by Lim et al. [28], who reported a surface area of 1,109 m\(^2\)/g from palm shells. Also, the surface area in this study is higher than that reported by Liu et al. [29], who prepared activated carbon with a surface area of 1,179 m\(^2\)/g from lotus stalks by H\(_3\)PO\(_4\) activation. The prepared activated carbon in this study has a pore surface area, pore diameter, pore volume, and micro-pore volume of 165.7 m\(^2\)/g, 1.93 nm, 1.23 m\(^3\)/g, and 1.17 m\(^3\)/g, respectively. In addition, the iodine adsorption number (1,043 mg/g) and methylene blue adsorption number (427 mg/g) measurements showed that the AMSAC was able to absorb small and large molecules equally well, suggesting the existence of a highly microporous structure.

The SEM images in Fig. 2 show the surface morphologies of AMSAC under two magnifications, 77x and 1,138x. It can be seen that AMSAC has an irregular fully solid structure with porous cavities distributed on its surface. The formation of the porous structure can result from evaporation and breakdown of the non-carbon compounds contained in the stem of the A. mauritanicus. Large and well-developed pores were clearly found on the surface of the activated carbon. The presence of the activator can enlarge the pores of activated carbon and expand its surface [30,31].

Fig. 3 shows the XRD pattern of the AMSAC sample. This activated carbon, which exhibits broad diffraction peaks and the absence of a sharp peak, reveals a predominantly amorphous structure [30,32]. There are two centered broad diffraction peaks around 2° = 23° and 44° in the spectrum.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g/mL)</td>
<td>0.255</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>6.72</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>9.63</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>30.5</td>
</tr>
<tr>
<td>Yield (%)</td>
<td>37.54</td>
</tr>
<tr>
<td>Iodine number (mg/g)</td>
<td>1,043</td>
</tr>
<tr>
<td>Methylene blue number (mg/g)</td>
<td>427</td>
</tr>
<tr>
<td>( S_{\text{BET}} ) (m(^2)/g)</td>
<td>1,293</td>
</tr>
<tr>
<td>Pore specific surface (m(^2)/g)</td>
<td>165.7</td>
</tr>
<tr>
<td>Total pore specific volume (cm(^3)/g)</td>
<td>1.23</td>
</tr>
<tr>
<td>Micropore volume (cm(^3)/g)</td>
<td>1.17</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>1.93</td>
</tr>
</tbody>
</table>

Table 1: Characterisation of AMSAC prepared by phosphoric acid

Fig. 2. SEM micrographs of AMSAC (A = 77x and B = 1,138x).
corresponding to the diffraction of (002) and (100), respectively. The appearance of the peak at around 23° at an activation temperature of 500°C signifies an increasing regularity of the crystalline structure, which will result in a better layer alignment [33]. The crystallinity recorded by AMSAC is 7.2% with 92.8% amorphous. These results were close to previous studies that used different lignocellulosic raw materials [33–35].

The FTIR spectrum of AMSAC (Fig. 4) shows an absorption band at 3,700–3,100 cm$^{-1}$, with a maximum at about 3,400–3,340 cm$^{-1}$, which is characteristic of the stretching vibration of the hydrogen-bonded hydroxyl of phenolic
groups [36]. The band at 2,800–3,000 cm\(^{-1}\) indicates the presence of an aliphatic C–H. The spectrum shows a small peak at 1,695–1,710 cm\(^{-1}\), according to Montes-Morán et al. [37], that can be assigned to the C=C symmetrical stretching of pyrone groups and C=O of carboxylic groups. The band at 1,000–1,300 cm\(^{-1}\) is usually found with oxidized carbons and has been assigned to C–O stretching in acids, alcohols, phenols, ethers, and/or esters groups [38]. In addition, the vibration bands located at 1,026 cm\(^{-1}\) can be ascribed to the stretching modes of Si–O–Si, representing the existence of silicate functional groups. Furthermore, the peaks at 680–700 cm\(^{-1}\) are an indication of Si–Si bonds [39].

3.2. Effect of time

Fig. 5 shows the results obtained from adsorption kinetics experiments with AMSAC. According to this plot, the PO\(_4^{3-}\) removal was characterized by a fast increase in PO\(_4^{3-}\) adsorption in the first 4 min of contact. This fast increase was due to the availability of a large number of vacant sites for adsorption during the initial stages. With the occurrence of the reaction, the number of active sites on the AMSAC decreases continuously, and the concentration gradient diminishes, finally reaching equilibrium. The equilibrium for phosphate ion adsorption onto the AMSAC was reached in approximately 45 min, with the maximum uptake removal of 4.5 mg/g. The data shown in Fig. 5 were used to determine kinetic parameters in the kinetic models tested.

3.3. Effect of initial phosphate ion concentration

The effect of initial PO\(_4^{3-}\) concentrations between 10 and 60 mg/L in the solutions on the rate of adsorption onto AMSAC was investigated. As shown in Fig. 6, with an increase in PO\(_4^{3-}\) concentration, the removal efficiency decreases from 84.43% at 10 mg PO\(_4^{3-}\)/L to 61.68% for the extreme concentration of 60 mg PO\(_4^{3-}\)/L with the same contact time, initial pH, and adsorption temperature. Generally, there are several adsorption steps involved in the transfer of a solute in adsorption dynamics: film diffusion, particle diffusion, and the interior surface sorption. An increase in the uptake rate to the maximum adsorption capacities was observed at lower concentrations of PO\(_4^{3-}\) ions, which demonstrated that the uptake of phosphate ions by the AMSAC surface was very fast (Fig. 6).

3.4. Effect of initial potential hydrogen

The dissociation constants pK\(_1\), pK\(_2\), and pK\(_3\) of H\(_3\)PO\(_4\) are 2.15, 7.20, and 12.33, respectively. Depending on the pH of the solution, PO\(_4^{3-}\) exists as H\(_3\)PO\(_4\), HPO\(_4^{2-}\), HPO\(_4^{3-}\), and PO\(_4^{3-}\). So, the adsorption of phosphate depends on the pH of the solution. Therefore, it is necessary to consider the different ionic species of phosphate when investigating the adsorption reaction. Fig. 7 shows the effect of initial pH on the removal of PO\(_4^{3-}\) by AMSAC. For pH < 6 and pH > 10, the removal is lower, and for 6 < pH < 10, the removal of PO\(_4^{3-}\) is higher and reaches a maximum percent of around 75% at pH = 6–7. A similar type of behavior has also been reported for the adsorption of phosphate ions from an aqueous solution on activated carbon [40,41]. At pH = 2, the PO\(_4^{2-}\) exists predominantly as H\(_3\)PO\(_4\), which is weakly attached to the sites of the adsorbent [42]. For 6 < pH < 10, prevalent species of PO\(_4^{3-}\), such as H\(_2\)PO\(_4^{3-}\) and HPO\(_4^{2-}\), are anionic in nature and are easily adsorbed onto the positive surface of the adsorbent. The low phosphate uptake for pH > 10 can be attributed to the competition of hydroxide ions with phosphate ions for adsorption sites. Furthermore, the negatively charged phosphate ions at high pH can also be attributed to electrostatic repulsion with the negatively charged AMSAC surface.

3.5. Adsorption kinetic

Kinetic studies are generally used to describe the rate and extent of the adsorption of the adsorbate onto the adsorbent and to control the residual time of the whole
adsorption process. Hence, the adsorption rate constant values for $\text{PO}_4^{3-}$ adsorption onto AMSAC were determined by curve fitting, with results as shown in Figs. 8–11. The constants are reported in Table 2. It can be seen that the experimental data fit better with the pseudo-second-order model, with a determination coefficient ($R^2$) of 0.998, compared with the first-order model, with an $R^2$ of 0.938. In addition, the equilibrium sorption capacities ($q_e$) calculated by the pseudo-second-order model were closer to the experimental values, and the Chi-square test was also carried out to support the best fitting adsorption model. Similar results have been reported for the adsorption of $\text{PO}_4^{3-}$ onto Leftover coal [43], commercial activated carbon [44], peat-based biosorbent [45], biosorbent lignocellulosic butanol residue [46], and peat [40]. On the other hand, the initial adsorption rate $\alpha$ and coefficient $\beta$ of activated energy of the Elovich model, as shown in Table 2, implies that the Elovich model is not suitable to describe the adsorption process compared with the other models mentioned above. In terms of the intra-particle diffusion model, it can be seen that the $R^2$ was 0.648 for the whole adsorption process, while it was 0.974 for the initial time of the adsorption process, which indicates that the intra-particle diffusion is the limiting step at the initial time of the adsorption process [47,48].

### 3.6. Adsorption isotherm

The Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich equations expressed in Eqs. (8), (11), (13), and (15) were used to evaluate these adsorption isotherm data. All available adsorption isotherm models are composed of certain constant values, which are assigned to specific surface
**Fig. 8.** Pseudo-first-order kinetic model of the adsorption of PO$_4^{3-}$ onto AMSAC.

\[ y = -0.343x + 0.539 \]
\[ R^2 = 0.938 \]

**Fig. 9.** Pseudo-second-order kinetic model of the adsorption of PO$_4^{3-}$ onto AMSAC.

\[ y = 0.222x + 0.108 \]
\[ R^2 = 0.997 \]

**Fig. 10.** Intraparticular kinetic model adsorption of PO$_4^{3-}$ onto AMSAC.

\[ Y = 0.181x + 3.679 \]
\[ R^2 = 0.974 \]

\[ y = 0.034x + 4.135 \]
\[ R^2 = 0.648 \]
behavior and used to compare the adsorption properties of the adsorbents against adsorbates [49]. The interaction of phosphate ions in the liquid phase and the AMSAC solid phase was described by Freundlich, Langmuir, Temkin, and Dubinin–Radushkevich isotherm models. The plots are presented in Figs. 12–15, and the relative parameters are listed in Table 3. It can be seen that all the isotherms showed a similar shape and were nonlinear over a wide range of aqueous equilibrium concentrations. It was observed from Table 3 that the Langmuir fitting plot with a determination coefficient of $R^2 = 0.976$ and nonlinear Chi-square test of $\chi^2 = 0.225$ fit the experimental data better than the Freundlich, Temkin, and Dubinin–Radushkevich isotherms. Since the Langmuir model is more suitable to describe the experimental data, this suggests that the sorbent surface has uniformly distributed homogenous surface adsorption sites available for the adsorbate ions. It also assumes that, during adsorption, the energy is uniformly distributed between the adsorbate surface and adsorbent molecules for monolayer adsorption regardless of the pH and the temperature effect [50]. The theoretical complete monolayer coverage of PO$_4^{3-}$ on AMSAC was calculated to be 4.17 mg/g compared to the experimentally determined value of 4.52 mg/g, and $K_L$ (Langmuir isotherm constant) was 1.498 L/mg. The sorption capacity of the AMSAC obtained in this study can be regarded as relatively high and could be compared to other materials.
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**Fig. 12.** Langmuir plot of adsorption for $\text{PO}_4^{3-}$ onto AMSAC.

**Fig. 13.** Freundlich plot for adsorption of $\text{PO}_4^{3-}$ onto AMSAC.

**Fig. 14.** Temkin plot for adsorption of $\text{PO}_4^{3-}$ onto AMSAC.
reported in the literature (Table 4). Also, according to the data presented in Table 3, the favorable Langmuir isotherm is observed for $R_L$ (the separation factor) values greater than 0 and lesser than 1. The low value of $R_L = 0.143$ indicates high and favorable adsorption of PO$_4^{3-}$ onto AMSAC [60].

4. Conclusion

Microporous activated carbons with a significant contribution of mesoporosity were obtained by H$_3$PO$_4$ activation of A. mauritanicus stems. Activated carbon developed a surface area of 1,292 m$^2$/g and a pore volume of 1.23 cm$^3$/g. The XRD, BET, and FTIR techniques confirmed the successful elimination of the major mineral fraction on the AC samples. In batch mode studies, the phosphate ion removal by AMSAC was influenced by solution pH, initial concentration, and contact time. At pH = 7, AMSAC can remove around 75% PO$_4^{3-}$ from the solution with an initial phosphate ion concentration of 40 mg/L and a temperature of 25°C. Among the models applied to fit the adsorption kinetic data, the pseudo-second-order rate equation allowed for a better reproduction of the experimental results. It is also worth noting that the application of the intra-particle diffusion model showed that this phenomenon is the only rate-controlling step during the first stage of batch-wise adsorption, which extended up to around 30 min when most of the PO$_4^{3-}$ uptake takes place. The Langmuir isotherm model fit the experimental equilibrium data well, indicating the homogeneity of the adsorptive sites on the AMSAC particle surface and monolayer adsorption. However, to compete with
other adsorbents, some modifications need to be made to enhance the efficiency of the AMSAC to remove phosphate ions. These modifications will be performed in future works.

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Symbols

-  $s_{BET}$ — The specific surface area calculated via BET equation, $\text{m}^2/\text{g}$
-  $q_m$ — Maximum adsorption capacity, $\text{mg/g}$
-  $q_e$ — Adsorption capacity at equilibrium, $\text{mg/g}$
-  $q_{eq}$ — Calculated amount, $\text{mg/g}$
-  $q_t$ — Adsorption capacity at time $t$, $\text{mg/g}$
-  $b$ — Temkin isotherm energy of adsorption, $\text{J/mol}$
-  $C_0$ — Initial concentration of adsorbate, $\text{mg/L}$
-  $C_e$ — Equilibrium concentration of adsorbate, $\text{mg/L}$
-  $K_L$ — Langmuir isotherm constant, $\text{L/mg}$
-  $K_C$ — Constant pseudo-first-order model
-  $K_S$ — Constant pseudo-second-order model
-  $K_D$ — Intra-particle diffusion rate constant, $\text{mg/(g min)}^{1/2}$
-  $C$ — Constant related to the thickness of the boundary layer, $\text{mg/g}$
-  $\alpha$ — Initial adsorption rate, $\text{mg/(g min)}$
-  $\beta$ — Desorption rate, $\text{mg/g}$
-  $K_{Dn}$ — Freundlich isotherm constants, $\text{mg/g}$
-  $R_s$ — Separation parameter
-  $\epsilon$ — Polanyi potential
-  $\chi^2$ — Chi-square test

$R^2$ — Correlation coefficient

$K_D$ — Dubinin–Radushkevich constant, $\text{mol}^2/\text{kJ}^2$

$E$ — Free energy, $\text{kJ/mol}$

$R$ — Universal gas constant, $8.314 \text{J/mol K}$

$T$ — Temperature, °C

References


