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Production and characterization of activated carbon based on coffee husk residue for phosphate removal in aqueous solutions

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Abstract. ZnCl₂-activated carbon was prepared using coffee husk for phosphate adsorption in aqueous solutions. Textural, morphological and structural analyses were carried out to characterize the produced materials. XRD detected the presence of ZnO in the activated carbon structure, and the measured nitrogen isotherm showed a micro-macroporous structure with 989 m²/g of specific surface area for this material. Phosphate equilibrium and kinetic experiments were conducted. Equilibrium data fit best to the Dubinin-Radushkevich model (r²≥0.96), with maximum adsorption capacities of 59.38 – 63.87 mg P/g in the pH range between 5 and 9. Intraparticle diffusion was the rate-limiting mechanism of the adsorption.

1. Introduction
Phosphorus is an essential nutrient for plant growth; however, an excess of this element can negatively affect water sources. Agriculture is the main important source of phosphorus production, with 90% of the total production in the world [1]. Phosphorus is found in drainage waters or sweep waters from agricultural fields to water bodies (surface or underground). Phosphorus contamination can cause different effects on the environment; however, the most common and hazardous is eutrophication [2]. Phosphorus is present in natural waters and wastewaters almost exclusively as phosphates in the chemical form of orthophosphates, condensed phosphates (pyro-, meta- and other polyphosphates) and
organically bound phosphates [3]. The United States Environmental Protection Agency (USEPA) has recommended that the maximum level of phosphorus in water should not exceed 50 µg/l [4].

Adsorption is a treatment process widely used in water and wastewater treatment. Different adsorbents have been produced using a wide range of low-cost raw materials or precursors. Even coffee husk has been used successfully as a raw material for activated carbon (AC) preparation to remove pollutants [5, 6]. Finding new raw materials to produce high-quality adsorbents is still a priority concern, and using adsorbents to remove inorganic pollutants such as phosphates from water is challenging. Thus, the present work aims to prepare an efficient adsorbent from coffee husk to remove phosphates from aqueous solutions.

2. Materials and Methods

2.1. Production and characterization of activated carbon

Activated carbon was produced using dried, ground and sieved (less than 0.5 mm particle size) coffee husk (CH). The raw material was mixed with ZnCl2 and carbonized at 600°C for 2 h in a nitrogen flow according to previous work [7, 8]. The activated material was washed repeatedly and sequentially with solutions of HCl, hot water and room temperature water. Finally, the produced activated carbon (C-CH) was dried, ground and sieved to reach particle sizes of less than 0.25 mm.

The prepared adsorbent was characterized by its morphological, textural and structural properties. Micrographs were obtained using a Zeiss (Germany) Ultra Plus field emission scanning electron microscope (FESEM) to evaluate morphological properties. A nitrogen isotherm (77 K) was built from nitrogen adsorption at different relative pressures (0 – 1) using a Micromeritics ASAP 2020 surface area analyzer. Specific surface area (SBET), mesoporous surface area (SMESO), net volume (VNET) and microporous volume (VMICRO) were calculated from the nitrogen isotherm via application of widely used models [9].

X-ray diffraction (XRD) analysis was carried out to determine the structural properties of the produced materials using a Siemens D5000 diffractometer operated at 30 kV and 20 mA. Raman spectra of the materials were obtained using a Horiba (Japan) Jobin-Yvon LabRAM HR800 high-resolution confocal µ-Raman system.

2.2. Phosphate adsorption tests

Equilibrium and kinetic batch experiments were conducted to test the phosphate adsorption capacity of the activated carbon made of coffee husk (C-CH). For the equilibrium experiments, different initial phosphate concentrations between 10 and 150 mg/l were used. The initial C-CH dose was 1 g/l, and the time of the test was 48 h. Nonlinear equations of the Langmuir [10], Freundlich [11], Redlich-Peterson [12] and Dubinin-Radushkevich [13] models were used to fit the equilibrium data. Table 1 depicts equations and parameters of the equilibrium models.

For the kinetic experiments, the initial concentration of the phosphate solution was 50 ppm, and 2 initial C-CH doses (1 and 2 g/l) were tested. The kinetic experiments were conducted without the initial pH modification, and samples for phosphate analyses were taken at the initial time and then at 5, 10, 15, 20, 30, 60, 90 and 120 min. The models used to fit the kinetic data were the pseudofirst order (PFO) [14], the pseudosecond [15] and the Elovich models [16]. Table 2 depicts equations and parameters of the kinetic models. All these models were used in their nonlinear versions.
Table 1. Nonlinear equations of the equilibrium models used in this study.

| Model              | Equation                                                                 | Parameters                                                                 |
|--------------------|--------------------------------------------------------------------------|---------------------------------------------------------------------------|
| Langmuir           | \( q_e = \frac{Q_{\text{max}}K_LC_e}{1+K_LC_e} \)                          | \( q_e = \text{amount of adsorbate uptake at equilibrium (mg/g)} \)          |
|                    |                                                                          | \( C_e = \text{adsorbate concentration at equilibrium (mg/L)} \)            |
|                    |                                                                          | \( Q_{\text{max}} = \text{maximum saturated monolayer adsorption capacity of the adsorbent (mg/g)} \) |
|                    |                                                                          | \( K_L = \text{constant related to the affinity between the adsorbent and adsorbate (L/mg)} \) |
| Freundlich         | \( q_e = K_F C_e^n \)                                                   | \( K_F = \text{Freundlich constant (mg/g)/(mg/L)} \)                       |
|                    |                                                                          | \( n = \text{Freundlich intensity parameter (dimensionless)} \)            |
| Redlich-Peterson   | \( q_e = \frac{K_{RP}C_e^n}{1+g}\)                                      | \( K_{RP} = \text{Redlich-Peterson constant (L/g)} \)                       |
|                    |                                                                          | \( g = \text{(dimensionless)} \)                                          |
| Dubinin-Radushkevich | \( q_e = q_{DR} e^{-k_{DR}t^2} \)                                       | \( q_{DR} = \text{adsorption capacity (mg/g)} \)                           |
|                    |                                                                          | \( k_{DR} = \text{constant related to the sorption energy (mol}^2/\text{kJ}) \) |
|                    |                                                                          | \( \epsilon = \text{Polanyi potential, calculated by the equation } \epsilon = RT\ln(1+1/C_e), \text{ where } R \text{ is the gas constant and } T \text{ is the temperature (in Kelvin)} \) |

Table 2. Nonlinear equations of the kinetic models used in this study.

| Model              | Equation                                                                 | Parameters                                                                 |
|--------------------|--------------------------------------------------------------------------|---------------------------------------------------------------------------|
| Pseudofirst order  | \( q_t = q_e(1 - e^{-k_1t}) \)                                           | \( q_t = \text{amount of adsorbate adsorbed per mass of adsorbent at time } t \ (\text{mg/g}) \) |
|                    |                                                                          | \( q_e = \text{amount of adsorbate adsorbed per mass of adsorbent at equilibrium (mg/g)} \) |
|                    |                                                                          | \( k_1 = \text{rate constant of the PFO equation (1/min)} \)                |
| Pseudosecond order | \( q_t = \frac{q_e^2 k_2 t}{1+k_2 q_e t} \)                             | \( k_2 = \text{rate constant of the PFO equation (g/mg x min)} \)          |
|                    |                                                                          | \( h = \text{initial adsorption rate (mg/g x min)}, h = k_2 q_e^2 \)       |
| Elovich            | \( q_t = \frac{1}{\beta \ln(1 + \alpha \beta t)} \)                     | \( \alpha = \text{initial rate constant (mg/g x min)} \)                   |
|                    |                                                                          | \( \beta = \text{desorption constant during the experiment (mg/g)} \)      |

The nonlinear equations of the equilibrium and kinetic models were solved using Origin Pro 2018b software.

Additionally, the intraparticle diffusion model was used to study the rate-limiting step of the process and to understand the mechanism of the process:

\[ q_t = k_{\text{diff}} \sqrt{t} + C \] (8)

where \( k_{\text{diff}} \ (\text{mg/g x min}^{0.5}) \) is the rate constant of the intraparticle diffusion model [17], and \( C \ (\text{mg/g}) \) is a constant associated with the thickness of the boundary layer. The curve \( q_t \ vs. \ t^{0.5} \) was drawn based on the kinetic curves, and the linear equation of the intraparticle diffusion model was applied for the three stages of adsorption: surface diffusion, intraparticle diffusion and equilibrium adsorption.
Phosphate as phosphorus (mg/l) was measured using the ascorbic acid method of the Standard Method for the Examination of Water and Wastewater [3] for both the kinetic and equilibrium experiments.

3. Results and Discussion

3.1. Production and characterization of activated carbon
The following figure depicts FESEM images of coffee husk as a raw material (figure 1a) and after carbonization (figure 1b). Obviously, the activated carbon shows a porous structure compared to that of the raw material, with different pore sizes and shapes. The pores of the activated carbon are mostly irregular; however, there are pores with circular and ovoid shapes, as well.

![Figure 1. FESEM images of raw material (a) and activated carbon (b) made of coffee husk.](image)

The nitrogen adsorption isotherm (figure 2a) for the produced adsorbent is mainly of type Ia, e.g., with a well-developed microporous structure [18]. However, the presence of a hysteresis loop (type H4) confirms that C-CH is mesoporous as well. Thus, the C-CH activated carbon consists of a micro-mesoporous structure.
Figure 2. (a) Nitrogen adsorption isotherm (77 K), (b) pore size distribution (PSD), (c) Raman spectrum, and (d) XRD analysis of the prepared material (o for activated carbon and * for ZnO phases).

The calculated textural parameters for C-CH are $S_{\text{BET}}= 989 \text{ m}^2/\text{g}$, $S_{\text{EXT}}=557 \text{ m}^2/\text{g}$, $V_{\text{NET}}=0.55 \text{ cm}^3/\text{g}$ and $V_{\text{MICRO}}=0.19 \text{ cm}^3/\text{g}$. The $V_{\text{MICRO}}/V_{\text{NET}}$ ratio of 34.5% shows that the material pore structure contains more pores in the mesoporous region (pores between 2 and 50 nm) than in the microporous region (pores less than 2 nm). The pore size distribution (PSD) (figure 2b) indicates that most mesopores are distributed between the pore diameter range of 2 – 10 nm, but no significant amount of mesopores exist between 10 - 50 nm.

The Raman spectrum (figure 2c) shows the two classical peaks for activated carbon at approximately 1339 and 1588 cm$^{-1}$, which correspond to the D and G bands, respectively. These two bands are typical for materials with an amorphous character with a structure dominated by nanocrystalline forms. The ratio $I_D/I_G = 0.77$ indicates that the structure of the adsorbent is disordered.

In the XRD data (Figure 2d), it is possible to identify two phases in the C-CH sample, the amorphous and crystalline phases. The amorphous phase corresponds to activated carbon graphite. The crystalline phase clearly corresponds to ZnO nanoparticles. ZnO evolves from the chemical activator ($\text{ZnCl}_2$) during the carbonization process and is trapped in the activated carbon structure or retained on its surface.

3.2. Phosphate adsorption capacity

Figure 3 depicts the phosphate adsorption isotherms of C-CH at three initial pH levels. The isotherms at different pH levels are similar, all starting with very low equilibrium adsorption ($q_e$) levels, and when the equilibrium concentration ($C_e$) increases, the adsorption capacity increases. However, the maximum equilibrium is not clearly reached in the experimental conditions (the initial phosphate concentration between 10 and 150 mg/l and C-CH dose of 1 g/l).
According to the parameters of the four applied models (see table 3) fit to the phosphate equilibrium adsorption data, the Dubinin-Radushkevich model gives the best fit: the correlation coefficient ($r^2$) is higher than 0.96, and the chi-square statistic ($X^2$) is between 6.21 and 14.09. The maximum amount of phosphate adsorbed by the unit of adsorbent calculated from these models is between 59.38 and 63.87 mg/g. Different authors, using biochar and activated carbon-based adsorbents for phosphate removal from water, report maximum adsorption capacities between 3.8 and 98.39 mg P/g [19-26].

Table 3. Parameters obtained for different models.

| Model                 | Parameter       | pH = 5       | pH = 7       | pH = 9       |
|-----------------------|-----------------|--------------|--------------|--------------|
| Langmuir              | $Q_{max}$ (mg/g) | $1.74 \times 10^5$ | $1.61 \times 10^5$ | $1.82 \times 10^5$ |
|                       | $K_L$ (l/g)     | $1.09 \times 10^{-5}$ | $1.19 \times 10^{-5}$ | $1.02 \times 10^{-5}$ |
|                       | $r^2$           | 0.80         | 0.81         | 0.78         |
|                       | $X^2$           | 52.15        | 49.26        | 57.78        |
| Freundlich            | $K_F$ (mg/g)/(mg/l)$^n$ | 0.19       | 0.17       | 0.18         |
|                       | $n$             | 1.92         | 1.98         | 1.96         |
|                       | $r^2$           | 0.93         | 0.94         | 0.93         |
|                       | $X^2$           | 17.23        | 16.05        | 19.38        |
| Redlich-Peterson      | $K_{RP}$ (l/g)  | 1.89         | 1.91         | 1.87         |
|                       | $a_{RP}$ (mg/l)$^g$ | 96.68   | -41.40       | 316.42       |
|                       | $g$             | -667.28      | 855.41       | -247.01      |
|                       | $r^2$           | 0.80         | 0.81         | 0.78         |
|                       | $X^2$           | 78.20        | 73.88        | 86.65        |
| Dubinin-Radushkevich | $q_{DR}$ (mg/g) | 59.38        | 63.87        | 60.14        |
|                       | $K_{DR}$ (mol$^2$/kJ$^2$) | 20.53   | 22.52       | 20.65        |
|                       | $r^2$           | 0.97         | 0.96         | 0.97         |
|                       | $X^2$           | 8.70         | 14.09        | 6.21         |
In the kinetic experiments, the equilibrium is visibly reached for the two C-CH doses of 1 and 2 g/l (figures 4a and 4b, respectively). The adsorption phenomenon is very fast during the first 20 min, and then the rate reduces. Equilibrium is reached during the first 40 min for both activated carbon loads.

Comparing the kinetic parameters for both activated carbon loads, the following observations can be drawn. When 1 g/l is used, the kinetic data fit best to the pseudofirst order model, and when 2 g/l is used, the kinetic data fit best to the pseudosecond order model. However, when both activated carbons are used, the kinetic data fit well to both models. Even when the activated carbon dose is 2 g/l, the kinetic data fit well to the Elovich model as well. This means that different adsorption mechanisms may influence the process, i.e., the initial concentration of nitrates can affect the diffusion inside the pores of the adsorbent and the chemical or physical interaction between the adsorbate molecules and the surface of the adsorbent.

The graphs of $q_t$ vs. $t^{0.5}$ for the intraparticle model are depicted in figures 4c and 4d for the samples with different initial loads. The three stages of the process in all experiments are identified and separated by the dotted lines. Table 4 shows the intraparticle model parameters. The parameters of the model are identified with the numbers 1, 2 and 3 for every stage of surface diffusion, intraparticle diffusion and equilibrium adsorption. The fact that the kinetic adsorption data fit very well to the intraparticle diffusion model indicates that intraparticle diffusion is the rate-limiting mechanism of the adsorption.
Table 4. Parameters of the different models used to fit the phosphate kinetic adsorption data of the produced adsorbents.

| Model          | Parameter   | AC load 1 g/l | AC load 2 g/l |
|----------------|-------------|---------------|---------------|
| Pseudofirst order | $q_i$ (mg/g) | 43.09         | 20.87         |
|                | $K_i$ (min$^{-1}$) | 0.129         | 0.211         |
|                | $r^2$       | 0.99          | 0.98          |
|                | $X^2$       | 3.220         | 1.14          |
| Pseudosecond order | $q_e$ (mg/g) | 47.20         | 22.62         |
|                | $K_2$ (g/mg min) | 0.004         | 0.010         |
|                | $h$         | 8.91          | 5.11          |
|                | $r^2$       | 0.98          | 0.99          |
|                | $X^2$       | 6.22          | 0.10          |
| Elovich        | $\alpha$   | 66.11         | 652.00        |
|                | $\beta$    | 0.15          | 0.46          |
|                | $r^2$       | 0.93          | 0.99          |
|                | $X^2$       | 0.22          | 0.44          |
| Intraparticle diffusion | $k_{Dif1}$ (mg/g min$^{0.5}$) | 10.44         | 5.89          |
|                | $C_i$ (mg/g) | -1.17         | 0.38          |
|                | $r_{i1}^2$  | 0.96          | 0.99          |
|                | $k_{Dif2}$ (mg/g min$^{0.5}$) | 1.84          | 1.13          |
|                | $C_i$ (mg/g) | 29.59         | 14.53         |
|                | $r_{i2}^2$  | 0.94          | 0.99          |
|                | $k_{Dif3}$ (mg/g min$^{0.5}$) | 0.30          | 0.33          |
|                | $C_i$ (mg/g) | 40.75         | 18.94         |
|                | $r_{i3}^2$  | 0.90          | 0.98          |

4. Conclusions
ZnCl$_2$-activated carbon was prepared using coffee husk for phosphate removal from aqueous solutions. XRD detected the presence of ZnO in the activated carbon structure, and the nitrogen isotherm presented a micro-macroporous structure with 989 m$^2$/g of specific surface area; however, the proportion of mesopores was higher than that of micropores. The equilibrium data fit best to the Dubinin-Radushkevich model ($r^2 \geq 0.96$), with maximum phosphate adsorption capacities of 59.38 – 63.87 mg P/g at different pH values. The kinetic data fit best to the pseudofirst and pseudosecond order models, indicating that the adsorption was influenced by different mechanisms; however, intraparticle diffusion was found to be the rate-limiting mechanism for the adsorption.

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