Fabrication of high surface area acid-treated activated carbon from pomegranate husk for 2,4-dichlorophenol adsorption

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Abstract

In the present study, zinc chloride followed by acid treating was employed for fabrication activated carbon with a high surface area from pomegranate husk (APHAC) for 2,4-dichlorophenol (2,4-DCP) adsorption. The APHAC was a well-developed pore and exhibiting specific surface areas of 1576 m$^2$/g. Based on the XRD analysis, the diffraction peaks between 15 ° and 35 ° corresponded to amorphous carbon, and the pHpzc values of APHAC was 6.15 ± 0.15. According to batch experiments, the optimum adsorption condition of 2,4-DCP was pH of 3, contact time 60 min, and APHAC dose of 1.75. The absorption capacity of 2,4-DCP at the APHAC dose of 0.5 promptly decreased from 259.5 ± 12.9 mg/g at the initial concentration of 150 mg/L to 74.5 ± 3.7 mg/g dose of 2 g/L. With increasing temperature from 10°C to 50°C, the adsorption efficiency declined from 99.8 ± 0.5% to 75.6 ± 1.89%. The isotherm and kinetic of 2,4-DCP by APHAC revealed that Freundlich and Elovich satisfactorily fitted with experimental data.

1. Introduction

One of the biggest concerns worldwide is water pollution. Phenolic compounds include many organic chemicals and are known as the most common water pollutants (Anisuzzaman et al. 2015). Industries such as pesticides, herbicides, plastics production, petroleum refineries, wood preservatives widely use chlorophenols (CPs). The CPs are often detected in surface water, landfill leachates, and industrial wastewaters (Okawa et al. 2004, Zou et al. 2009). 2,4-dichlorophenol (2,4-DCP) is a CPs that suspected to be endocrine disruptors and listed as one of the 65 priority pollutants by the US Environmental Protection Agency (Okawa et al. 2004). The 2,4-DCP widely used in pharmaceuticals and fungicides and has possessed great attention nowadays (Zhang et al. 2020). The 2,4-DCP is corrosive and can damage the kidneys, liver, lungs, skin, and digestive tract for humans, and it may also cause pathological symptoms (Pang et al. 2020). The 2,4-DCP has chlorine functional groups that make it a refractory compound in water resources and toxic for microorganisms because of chlorophenol's aromatic structure (Badu Latip et al. 2020). Due to the adverse of the 2,4-DCP on aquatic life and human health, its removal from water and wastewater is essential (Sadrnourmohamadia et al. 2017).

Some chemical and physical methods such as photocatalytic oxidation (Zhu et al. 2020), chemical oxidation (Sadrnourmohamadia et al. 2017), ion exchange (Nezamzadeh-Ejhieh &Ghanbari-Mobarakhe 2015), Fenton and electro-Fenton (Zhang et al. 2015), and biological degradation (Kargi &Eker 2005) have been studied for treating wastewater containing the 2,4-DCP. Some limitations for these methods are high-energy consumption, the lengthy-time required to produce excess sludge and secondary pollutants, and high cost (Badu Latip et al. 2020, Umar et al. 2010).

One of the frequently and effective methods for the phenolic compound’s removal from aqueous solution is adsorption. The adsorption is a process based on the bulk of the solution's contact with a solid phase, which can adsorb the solutes dissolved in the solution phase selectively (Shaarani &Hameed 2010). One of the main drawbacks of applying activated carbon (AC) is AC’s high price, limiting its application to a
full scale; thermally and chemically treated palm pith carbon, rice husk, and maize cob carbon have been used in the literature for 2,4-DCP removal (Akhtar et al. 2006). The type of activation processes, precursors, and thermal treatment procedures used in AC production can affect AC’s existing functional groups responsible for adsorbing pollutants from solutions (Heidarinejad et al. 2020).

Therefore, this study aimed to synthesize high surface area acid-treated AC from pomegranate husk (APHAC) and investigate its performance toward the 2,4-DCP removal from aqueous media, optimizing the influencing parameters including the initial concentration of 2,4-DCP, the initial pH of the 2,4-DCP solution, APHAC dose, and contact time. Furthermore, to determine the adsorption mechanism, the isotherm adsorption, reaction kinetics, and ionic strength effect for 2,4-DCP removal using APHAC were explored.

2. Materials And Methods

2.1. Chemical and reagent

The 2,4-DCP (CAS 120-83-2, chemical formula 2,4-(Cl)\textsubscript{2}C\textsubscript{6}H\textsubscript{3}OH) was purchased from Merck (Germany). During adsorption experiments, all the working solutions were prepared by dissolution of chemicals in deionized water.

2.2. Preparation of APHAC

The collected pomegranate husks (PHs) (Isfahan, Iran) were washed with tap water several times. The PHs were pulverized and sieved after drying for 12 h at 105 °C. The following procedure was used for APHAC fabrication: dissolve 100 g of ZnCl\textsubscript{2} in 50 mL of deionized water and add mixed with 100 g of PH, manually stirred under heating 70-80°C. The resulting paste was dried for 4 h at 105°C in a furnace, and afterward, the dried paste was transferred to the stainless-steel reactor and heated from room temperature to 600 °C at 10 °C/min for 30 min under the flux of N\textsubscript{2} (150 mL/min) (Leite et al. 2018, Lima et al. 2019b). After that, a 10.0 g of carbonized material and 200 mL of HCl (6 M) was placed in a 500 mL boiling flask; the mixture was stirred on a magnetic stirrer and reflux for 2 h at 70-80°C (Ribas et al. 2014, Thue et al. 2016). The slurry was cooled down and filtered, washed with deionized water several times, milled, sieved, and stored in an airtight container until use. The adsorbent was named acid-treated pomegranate husk activated carbon (APHAC).

2.3. Experiments of 2,4-DCP adsorption

The experiments of 2,4-DCP adsorption by APHAC were carried out in a batch system. The variables of the adsorption process including pH of the solution (3-9), APHAC dose (0.5-2 g/L), contact time (2-120 min), initial concentration of 2,4-DCP (50-150 mg/L), temperature (10-50 °C), and ionic strength (0.01-0.5 M) were investigated to determine the optimum adsorption conditions. The test solutions were mixed at 200 rpm to provide contact between APHAC particles and 2,4-DCP.
2.4. Analysis

The 2,4-DCP concentration in the solutions was quantified by a visible spectrophotometer (DR2000, Hach Company) at 510 nm. Eqs. (1) and (2) were employed for the calculation of adsorption efficiency and capacity.

See formulas 1 and 2 in the supplementary files.

Where $%_{\text{Removal}}$ and $q$ are the removal percentage and sorption capacity, respectively, $C_0$ and $C_f$ are, respectively, the influent and effluent concentrations (mg/L), $V$ is the solution volume (L), and $m$ is the sorbent mass (g).

3. Results And Discussion

3.1. Characteristics of APHAC

The values of specific surface area ($S_{\text{BET}}$) and total pore volume ($V_{\text{total}}$) were obtained from BET and BJH analysis (Fig. 1).

Fig. 1. $N_2$ adsorption and desorption isotherms, (inset) pore size distribution curve

The $V_{\text{total}}$ and $S_{\text{BET}}$ of APHAC were 0.83 cm$^3$/g and 1576 m$^2$/g, respectively, and confirmed a high surface area of APHAC. The high surface area of APHAC was mainly related to the application of ZnCl$_2$ and activating agent and acid leaching. Thue et al. (Thue et al. 2016) prepared the AC from wood chips by applying microwave and reported that $S_{\text{BET}}$ of obtained AC decreased from 914.08 m$^2$/g to 874.72 m$^2$/g with increasing inorganic: organic ratio from 1:1 to 1:1.5. Also, Hadi et al. (Hadi et al. 2020b) fabricated AC from PH by dual chemical activation and reported that $S_{\text{BET}}$ and $V_{\text{total}}$ of AC were 811.12m$^2$/g and 0.404 cm$^3$/g, respectively.

The XRD pattern of APHAC is displayed in Fig. 2.

Fig. 2. XRD pattern of APHAC

As illustrated, the broadbands ranging from 15° to 25° and 35° to 50° are corresponded to amorphous carbon and indicating that the acid leaching led to inorganic matter leaching from APHAC structure and prepared the carbon material with more amorphous pore walls, low crystallinity, and higher superficial area and pores structure. Similar results were reported by Ribas et al. (Ribas et al. 2014), who prepared AC from a cocoa shell with 6.0 M of HCl leaching for the reactive violet 5 dye removal from aqueous solutions and exhibited that amorphous carbon.

The FTIR spectrum of APHAC is illustrated in Fig. 3.

Fig. 3. The spectrum of FTIR of APHAC
As illustrated in Fig. 3, the band at 3432 cm$^{-1}$ is ascribed to OH stretching (Thue et al. 2020), and the band at 2929 cm$^{-1}$ was presumably related to the C-H vibrations in methyl and methylene groups (Baccar et al. 2009). The carboxylic acids or O=C stretching in esters was detected at 1637 cm$^{-1}$ (Lima et al. 2019a). The band located at 1386 is ascribed to the -CH band (Umpierres et al. 2018). The C–O stretching of phenolic or carboxylate Groups cause a band's emergence at 1023 cm$^{-1}$ (Saucier et al. 2015). The vibrational band of C-H out-of-plane of aromatics presented two bands at 637 and 470 cm$^{-1}$.

The elemental analysis of precursor PH and APHAC are summarized in Table 1.

**Table 1: Composition of precursor PH and APHAC**

| Material     | Element (%) |
|--------------|-------------|
|              | C    | H    | N    | S   |
| Precursor PH | 46.52 | 2.73 | 0.72 | 0.15|
| APHAC        | 83.23 | 0.89 | 2.02 | 0.13|

As present in Table 1, the APHAC was comprised of C (83.23%), H (2.19%), N (2.02%), and S (0.13%) and demonstrating the synthesis of APHAC leads to increasing the C and N content due to pyrolysis of raw material and leaching processes. The higher C content of APHAC suggests that the predominant structure of APHAC is aromatic (Thue et al. 2020). A similar trend was reported by Hadi et al. (Hadi et al. 2020b), who investigated the fabrication of AC from PH by dual chemical activation and established that the C content of AC improved from 46.52 to 62.05% when converted to AC.

An SEM photograph of APHAC is shown in Fig. 4.

Fig. 4. SEM photo of APHAC

SEM micrograph of APHAC reveals rough surface morphology, and its surface shows an aggregate of several particles with a mean particle size of 74.4 ± 6.3 nm.

Fig. 5 presents the variation of pH$_{pzc}$ by changing the APHAC dose.

Fig. 5. Variation of pH$_{pzc}$ as function APHAC dose

As seen in Fig. 5, the pH$_{pzc}$ values of APHAC were 6.17, 6.0, and 6.29 with the application of 0.1, 0.2, and 0.4 g/L, respectively. The various values of pH$_{pzc}$ were reported in the literature (Hadi et al. 2020a, Hadi et al. 2020b, Ribas et al. 2014). Umpierres et al. (Umpierres et al. 2018) studied microwave application for AC preparation from tucumá seed and reported that the pH$_{pzc}$ value was varied from 4.44 to 6.71. Ribas et al. (Ribas et al. 2014) reported that the value of pH$_{pzc}$ was ranging from 2.35 to 7.31. The pH$_{pzc}$ (Fig. 7) implies that at solution pH lower than 3.3, the APHAC has a positive surface charge, and higher than 3.3, the surface charge reverses to negative.
3.2. Adsorption of 2,4-DCP by APHAC

3.2.1. Effect of pH of the solution

To find performance adsorption of 2,4-DCP by APHAC under various solution pH, a series of the batch experiment were conducted at an initial 2,4-DCP concentration of 50 mg/L with different pH (Fig. 6).

Fig. 6. The removal performance of 2,4-DCP by APHAC under various pH (Concentration of 2,4-DCP: 50 mg/L, dose of APHAC: 0.5 and 0.75g/L, and contact time: 60 min)

As can be seen, with enhancing pH from 3 to 9, the performance of 2,4-DCP adsorption was reduced. When solution pH increased from 3 to 9, the performance of 2,4-DCP adsorption descended from 91.7 ± 4.6% to 73.5 ± 3.7 and from 93.3 ± 4.7% to 88.5 ± 4.4 with the application of 0.5 and 0.75 g/L of APHAC, respectively. As previously mentioned, the pKₐ values of 2,4-DCP were 7.44 (Kuśmierek et al. 2016), and the obtained pHpzc of APHAC was 6.15 ± 0.15, and its surface is protonated form at pH values < 7.44 and negatively charged at pH values > 7.44. The drop in the removal percentage for values of pH > 7.45 is explained by electrostatic repulsion of both negatively charged (adsorbent and adsorbate). On the other hand, there is a small decrease in removal from pH 3-7. The maximum adsorption occurs at pH 3, where the adsorbent is positively charged, and the adsorbate is presented in the protonated form. This circumstance demonstrates that the adsorption process’s dominant mechanism was the interaction between the organophilic nature of the APHAC surface and undissociated OCs (Shaarani &Hameed 2010). Kalderis et al. (Kalderis et al. 2017) studied the 2,4-DCP adsorption by biochar and reported that the optimum solution pH was 2.

3.2.2. Effect of contact time and kinetic study

The contact time has a significant influence on the adsorption process. The variation of 2,4-DCP adsorption efficiency by APHAC was studied at contact time 2 to 120 min and displayed in Fig. 7.

Fig. 7. Variation of 2,4-DCP removal by APHAC as a function of contact time (2,4-DCP: 50-150 mg/L, solution pH: 3, dose of APHAC: 0.5 g/L, and contact time: 2-120 min)

As observed, overall, the 2,4-DCP adsorption efficiency enhanced with increasing contact time. At various studied initial 2,4-DCP concentration, the highest amount of the 2,4-DCP adsorption occurred within the first 15 min, and after 15 min the rate of adsorption was a slowdown and reached equilibrium at 60 min, and 92.9 ± 1.9%, 87.2 ± 1.7%, and 83.2 ± 1.7% of 2,4-DCP was adsorbed at 50, 100, and 150 mg/L of 2,4-DCP, respectively. With further growth of the contact time, the adsorption efficiency is almost unchanged. The initial rapid adsorption of 2,4-DCP may be attributed to specific active surface sites and functional groups in the adsorptive process (Mohan et al. 2007).

To realize the amount of 2,4-DCP removed from the aqueous solution based on the contact time, the study of kinetic adsorption is critical. In the present work, four frequent kinetic were studied. The studied kinetic equations are summarized in Supplementary Table S1. Fig. 8 shows the kinetic curves of 2,4-DCP
adsorption on APHAC at different initial 2,4-DCP concentrations, and the kinetic parameters are summarized in Table 2.

Fig. 8. Kinetic of 2,4-DCP adsorption by APHAC

Table 2: Constant of the kinetics of 2,4-DCP adsorption by APHAC

| Kinetic models          | Parameter     | Initial 2,4-DCP concentration (mg/L) | 50      | 100      | 150      |
|------------------------|---------------|--------------------------------------|---------|----------|----------|
|                        |               |                                      |         |          |          |
| Pseudo-first order     | $q_e$ (mg/g)  |                                      | 86.49 ± | 163.2 ±  | 226.1 ±  |
|                        |               |                                      | 2.65    | 4.732    | 10.33    |
|                        | $k_f$ (min$^{-1}$) |                                  | 0.3688 ± | 0.2386 ± | 0.2168 ± |
|                        |               |                                      | 0.0764  | 0.0404   | 0.0560   |
|                        | $R^2_{adj}$   |                                      | 0.9139  | 0.9353   | 0.8494   |
| Pseudo-second order    | $q_e$ (mg/g)  |                                      | 91.51 ± | 175.4 ±  | 245.2 ±  |
|                        |               |                                      | 1.92    | 2.925    | 9.048    |
|                        | $k_s$ (g/(mg.min)) |                                | 0.0063 ±| 0.0021 ±| 0.0013 ±|
|                        |               |                                      | 0.0012  | 0.0002   | 0.0003   |
|                        | $R^2_{adj}$   |                                      | 0.9717  | 0.9871   | 0.9359   |
| Elovich                | $a$ (g/(mg.min)) |                                | 1757.5 ±| 556.4 ±  | 528.4 ±  |
|                        |               |                                      | 811.5   | 193.5    | 177.9    |
|                        | $\beta$ (g/mg) |                                      | 0.1034 ±| 0.0432 ±| 0.0292 ±|
|                        |               |                                      | 0.0064  | 0.0027   | 0.0019   |
|                        | $R^2_{adj}$   |                                      | 0.9917  | 0.9871   | 0.9843   |
| Avrami fractionary     | $q_e$ (mg/g)  |                                      | 101.73 ±| 180.5 ±  | 372.4 ±  |
|                        |               |                                      | 6.647   | 5.093    | 164.7    |
|                        | $k_{AV}$ (min$^{-1}$) |                           | 0.2229 ±| 0.1703 ±| 0.0163 ±|
|                        |               |                                      | 0.0851  | 0.0236   | 0.045    |
|                        | $n_{AV}$      |                                      | 0.2996 ±| 0.4403 ±| 0.2717 ±|
|                        |               |                                      | 0.0502  | 0.0432   | 0.0818   |
|                        | $R^2_{adj}$   |                                      | 0.9931  | 0.9937   | 0.9845   |

As summarized in Table 2, all kinetic models can satisfactorily describe the 2,4-DCP adsorption data. However, based on the $R^2_{adj}$, the Elovich and Avrami-fractional model were the best models. As can be seen, the value of $q_e$ improved with increasing initial 2,4-DCP concentration.

3.2.2. Effect of APHAC dose and isotherm study

The adsorption of 2,4-DCP onto APHAC was measured at seven different doses of adsorbent at solution pH of 3 and contact time of 60 min and 50-150 mg /L of 2,4-DCP to investigate the influence of sorbent dose. The results of the adsorption experiments are shown in Fig. 9.
Fig. 9. (a) adsorption efficiency and (b) sorption capacity as function of APHAC dose (2,4-DCP: 50-150 mg/L, solution pH: 3, APHAC dose: 0.5-2.0 g/L, and contact time: 60 min)

It is clear that the adsorption performance of 2,3-DCP by APHAC was improved from 92.9 ± 3.7% to 99.8 ± 0.5%, from 90.2 ± 3.6% to 99.1 ± 0.5, and from 86.5 ± 3.5 to 99.3 ± 0.5% with increase in APHAC dose from 0.5 to 2.0 g/L for 50, 100, and 150 mg/L of 2,4-DCP, respectively. When the APHAC dose increased, the number of active sites for adsorption increased, and as a result, the higher amount of 2,4-DCP molecule can be adsorbed to the adsorption sites. The same trend is reported by others (Daware & Gogate 2020, Kalderis et al. 2017, Namasivayam & Kavitha 2005).

3.2.3. Effect of ionic strength

To investigate ionic strength's effect, the adsorption performance of 2,4-DCP dye onto APHAC was investigated at various ionic strengths (0.01-0.5M) and two constant doses of APHAC (1 and 1.75 g/L). The adsorption efficiency of 2,4-DCP as a function of ionic strength is given in Fig. 10.

As shown in Fig. 10, the APHAC adsorption performance declined from 98.2 ± 0.3 % to 87.5 ± 2.6% and from 99.8 ± 0.1% to 95.5 ± 2.9% with application 1 and 1.75 g/L of APHAC when the ionic strength is changed from 0.01 to 0.5 M in the presence of salinity, two mechanisms can interfere on the adsorption process including compressing the double electric layer and leading to electrostatic repulsion of the sorbent molecules from the sorbate surface and the competition between the cationic ions and consequently dropping the surface electrostatic potential (Silva et al. 2020). Besides, the Na$^+$ ions can attract with π-electrons and lead to the formation of the positive electric layer, and as a result, the sorbent is surrounded by Cl$^-$ ions, and then a diffuse layer of solvated ions is formed and lead to the reduction of adsorption performance (Bernal et al. 2020). As Bernal et al. (Bernal et al. 2020) mentioned, the adsorption performance reduction can be related to the increasing of Na$^+$ concentration and its competition with acetaminophen for the adsorption sites.

3.2.5. Adsorption temperature

To study the effect of temperature, the 2,4-DCP adsorption experiments by APHAC was performed at a temperature in the range of 10-50 °C (Fig. 11).

As can be observed in Fig. 11, the adsorption efficiency of 2,4-DCP reduced with increasing temperature. The temperature increment from 10 to 50 °C led to a sharp decrease in adsorption efficiency from 99.8 ± 0.5% to 75.6 ± 1.89%. Theoretically, when the solution's salinity is enhanced, the adsorption capacity is reduced due to the attractive electrostatic forces between adsorbate molecules and the adsorbent
surface. Conversely, when the ionic strength increased, the adsorption efficiency improved because of the repulsive electrostatic forces (Al-Dege et al. 2008). Hadi et al. (Hadi et al. 2020b) found that the adsorption of 4-chlorophenol declined from 75 to 33% with increasing ionic strength from 0 to 0.3 M.

3.2.6. Isotherm study

Here, three models, including Liu, Freundlich, and Langmuir model, were used to describe how 2,4-DCP interact with APHAC at two doses of APHAC (Supplementary Table S2). Fig. 12 displays the nonlinear isotherms plot of 2,4-DCP using APHAC and obtained constants summarized in Table 3.

Fig. 12. Fitted isotherm of 2,4-DCP adsorption by APHAC

| Table 3: Parameters of isotherm models |
|----------------------------------------|
| Model       | Parameter | APHAC dose (g/L) |
|             |           | 1 | 1.75 |
| Freundlich  | $K_F$ (mg/g. (mg/L)$^{-1/n_F}$) | 34.29 ± 3.03 | 55.74 ± 3.89 |
|             | $1/n_F$   | 0.6259 ± 0.0651 | 0.4059 ± 0.1511 |
|             | $R^2_{adj}$ | 0.9954 | 0.9889 |
| Langmuir    | $Q_{max}$ (mg/g) | 648.8 ± 62.12 | 256.9 ± 23.39 |
|             | $K_L$ (L/mg) | 0.0277 ± 0.0046 | 0.1436 ± 0.0368 |
|             | $R^2_{adj}$ | 0.9913 | 0.9659 |
| Liu         | $Q_{max}$ (mg/g) | 1774.8 ± 188.2 | 1215.2 ± 228.8 |
|             | $K_g$ (L/mg) | 0.0034 ± 0.0021 | 0.0012 ± 0.0071 |
|             | $n_L$     | 0.7184 ± 0.1259 | 0.4588 ± 0.1137 |
|             | $R^2_{adj}$ | 0.9959 | 0.9875 |

Comparing to Langmuir and Liu isotherm, the highest $R^2_{adj}$ are related to Freundlich isotherm and indicating a better fit. The Freundlich isotherm assumes that the adsorbate amount on the adsorbent surface increases as the adsorbate concentration increases (Bergmann & Machado 2015) and confirm the obtained data.

4. Conclusion
A high surface AC was prepared from PH using ZnCl$_2$ as a chemical activating agent and used for 2,4-DCP adsorption from the aqueous solution. The APHAC has a specific surface area of 1576 m$^2$/g, and the surface of APHAC was neutral at a pH value of 6.15 ± 0.15. Batch experiments carried out on the APHAC-2,4-DCP sorption system indicated varied 2,4-DCP adsorption efficiency. The results showed that to decline the adsorption performance with increasing pH of the solution, initial 2,4-DCP concentration, and temperature. However, the adsorption efficiency of 2,4-DCP was further governed by the dose of APHAC. The APHAC-2,4-DCP interaction indicated a good fit with Elovich chemisorptions and the Freundlich isotherm. The isotherm, the $Q_{\text{max}}$, is very high for APHAC and is 648.8 ± 62.1 mg/g and 256.9 ± 23.4 mg/g with the application of 1 and 1.75 g of APHAC, respectively.

**Declarations**

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**Ethical Approval**

All procedures performed in study were in accordance with the ethical standards of the Iranian national research committee and its later amendments or comparable ethical standards.

**Consent to Participate**

The manuscript is an original work of all authors and all authors made a significant contribution to this study.

**Consent to Publish**

The authors hereby consent to publication of the work in Environmental Science and Pollution Research journal.

**Authors Contributions**

**Ensiyeh Taheri**: Investigation, Data curation, Formal analysis, Writing- Original draft preparation; **Mohammad Mehdi Amin**: Data curation, Writing- Original draft preparation; **Ali Fatehizadeh**: Conceptualization, Supervision, Methodology, Writing - Original draft preparation; **Eder C. Lima**: Software, Writing - Review & Editing.

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**Competing Interests**
The authors declare no conflict of interest

**Availability of data and materials**

Nill

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