

## Evaluation of the adsorption of perfluorooctanoate (PFOA) onto customized ordered mesoporous carbon (OMC): adsorption behaviors and mechanisms

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### Highlights:

- Ordered mesoporous carbon (OMC) was first used for PFOA adsorption.
- The oxygen content effects of OMCs on PFOA adsorption were first studied.
- Fluoride anion and divalent cations can improve the PFOA adsorption capacity significantly.
- The main adsorption mechanisms are hydrophobic interaction and electrostatic attraction.

Keywords: OMC, PFOA, Oxygen content.

## INTRODUCTION

Perfluorooctanoic acid (PFOA or C8) has been extensively used in industry and consumer products worldwide such as paper, leather, textile coatings, and firefighting foams production. Due to the lack of treatment in the past decades, PFOA is continuously exposed ubiquitously in various water bodies. As a result, drinking water has become one of the major sources of human exposure to PFOA all over the world [1]. Adsorption has exhibited unique advantages such as technological maturity and ease of operation, and the adsorption process is widely used in practical applications including wastewater and drinking water treatment [2]. Thus, adsorption is considered a further developing yet suitable treatment technique for PFOA removal from water. Due to the low costs and a wide range of manufacturing resources, carbon-based materials are widely utilized as adsorbents for PFOA removal. Examples include granular activated carbon (GAC), and powdered activated carbon (PAC) [3]. However, activated carbons with large particle sizes exhibited slow adsorption rates due to their intra-particle diffusion limitations, and their adsorption capacities are low due to their limited surface hydrophobic functional groups. Therefore, OMC, a carbon-based material with a high specific surface area, large amount of mesoporous, and high hydrophobicity could be a potential candidate adsorbent for PFOA removal from aqueous solutions [3].

## METHODOLOGY

Surfactant Pluronic P123 and silicon source TEOS were used for mesoporous SBA-15 (Nano-SiO<sub>2</sub>) template preparation. Then, sucrose was used as the carbon source for OMC preparation. OMCs with different oxygen contents were prepared under different pyrolysis temperatures (500 – 1100°C). The details of the synthesis procedure are shown in **Figure. 1**.

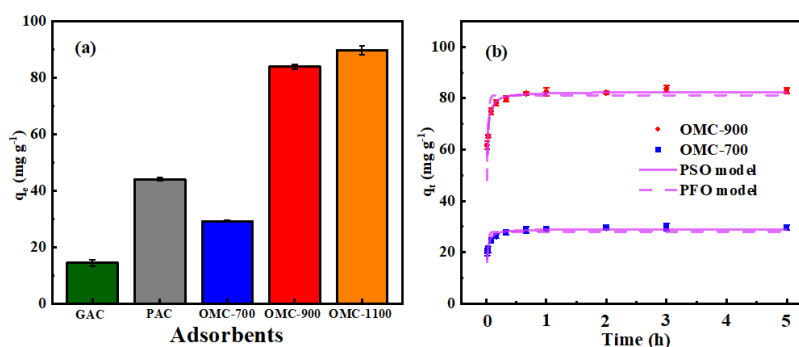


**Fig. 1.** Step-by-step synthesis of OMC.

Batch adsorption experiments were conducted to evaluate the adsorption capacity of PFOA onto OMCs. Ten mg OMCs were added in 100 mL PFOA solutions, the initial and final PFOA concentrations were analyzed by Agilent 1100 High-performance liquid chromatography (HPLC) with Agilent 6340 Ion Trap (MS step).

## RESULTS AND CONCLUSIONS

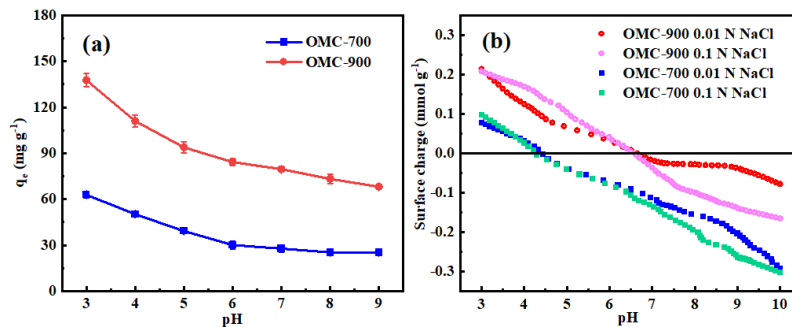
OMC-900 had almost a fivefold higher adsorption capacity over the GAC and a twofold improvement over the PAC (**Figure 2a**). The adsorption equilibrium was reached within 1 h (**Figure 2b**). The OMC-900 showed a higher adsorption capacity for PFOA than that of OMC-700. The increase in carbonization temperature caused a decrease in the O/C ratio from 0.17 (OMC-700) to 0.11 (OMC-900). The low O/C ratio reflects the high hydrophobicity of OMCs. Hydrophobic interaction is involved in adsorbing PFOA onto OMCs [4].



**Fig. 2** (a) Adsorption capacities comparison (b) kinetic study

The adsorbed amounts of PFOA decreased continuously from pH 3.0–9.0 (**Figure 3a**). The surface charges at different solution pH values are shown in **Figure 3b** and the point of zero charge ( $pH_{pzc}$ ) of OMC-900 is higher than OMC-700 due to the less oxygen-containing groups. The more positively charged OMC-900 explains its higher adsorption capacity than OMC-700 under the same pH value. Due to the anionic property of PFOA in water and the positive surface charge of the OMCs in the pH range studied, electrostatic attraction might occur between the adsorbates and the adsorbents.

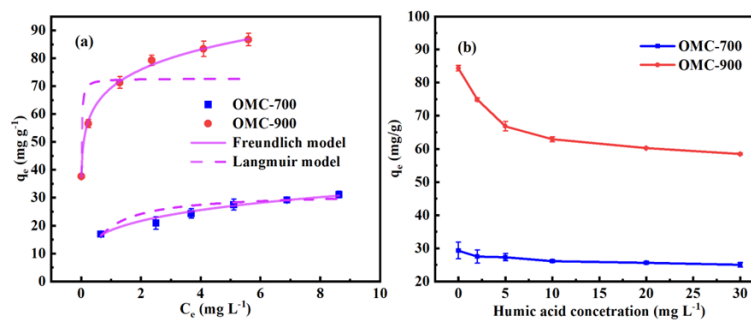
Although the electrostatic repulsion prevented the adsorption of PFOA onto the negative OMC-900 at a high pH value, the adsorbed amounts are still higher than the positively charged OMC-700 (**Figure 3a**). Indicating that hydrophobic interaction could overcome the electrostatic repulsion during the adsorption process.



**Fig 3** (a) pH effect on adsorption of PFOA on OMCs (b) Point of zero charge ( $pH_{pzc}$ ) of OMCs

As expected, the adsorbed amounts of PFOA increased with the increase of their equilibrium solute concentrations (**Figure 4a**). OMC-900 shows a much better adsorption performance towards PFOA than OMC-700. The significant decrease of adsorbed amounts of PFOA by OMC-700 compared with OMC-900 is attributed to the more oxygen-containing functional groups on the OMC-700 surface, including -OH and -COOH groups. The experimental data were found to be a better fit for the Freundlich model, indicating the absorption of PFOA onto OMCs is multilayer adsorption.

**Figure. 4(b)** shows the effects of humic acid (HA) on the absorption of PFOA onto OMCs. The HA can compete with PFOA for the adsorbent sites on the adsorbent surface even when the adsorbent is negatively charged, the PFOA adsorption capacity could be reduced because of the limited hydrophobic surface on OMCs.



**Fig. 4** (a) Isotherm study of adsorption PFOA on OMCs (b) HA effect on adsorption PFOA on OMCs

OMC-700 and OMC-900 with different oxygen contents were prepared under different calcination temperatures. The adsorption equilibrium of PFOA on both OMCs was achieved within 1 h. OMC-900 with an adsorbed capacity of 82.9 mg g<sup>-1</sup> for PFOA at pH 6.0, which was much higher than that of OMC-700 (29.6 mg g<sup>-1</sup>), indicating that oxygen content plays an important role in PFOA adsorption. Humic acid, considered an organic matter surrogate, caused the PFOA adsorption capacity to decrease dramatically. The study results show that hydrophobic interaction and electrostatic interaction are the main adsorption mechanisms of PFOA onto OMCs.

## ACKNOWLEDGMENTS

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