Exploring PFOA adsorption isotherm in the presence of NOM using DBD plasma-modified GAC

Thera Sahara1, Doonyapong Wongsawaeng1,*, Kanokwan Ngaosuwan2, Worapon Kiatkittipong3, Peter Hosemann4, Suttichai Assabumrungrat5,6

1Research Unit on Plasma Technology for High-Performance Materials Development, Department of Nuclear Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
2Division of Chemical Engineering, Faculty of Engineering, Rajamangala University of Technology Krungthep, Bangkok 10120, Thailand
3Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand
4Department of Nuclear Engineering, Faculty of Engineering, University of California, Berkeley, 94720, U.S.A.
5Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Chulalongkorn University, Bangkok 10330, Thailand
6Bio-Circular-Green-economy Technology & Engineering Center (BCGeTEC), Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand 10330

Abstract. Perfluorooctanoic acid (PFOA), a widely used perfluorinated alkyl substance (PFAS), poses significant environmental and health risks. This study investigates PFOA adsorption in the existence of natural organic matter (NOM) using granular activated carbon (GAC) modified with dielectric barrier discharge (DBD) plasma. PFOA's amphiphilic structure, characterized by a hydrophilic carboxyl group head and a hydrophobic perfluorinated tail, contributes to its versatility and persistence. The selection of the Chao Phraya River (CPR) water as the NOM source, captures the complexity of a major water body subjected to diverse pollution sources. The results were analyzed through the Toth and Temkin isotherm models. Application of the Toth isotherm model reveals enhanced PFOA adsorption capacity in CPR water compared to DI water, emphasizing the influence of NOM. The Temkin isotherm analysis further characterizes the strength and efficiency of the adsorption process, highlighting a stronger interaction between PFOA and plasma-modified GAC in CPR water. The study indicates that the adsorption process in CPR water may be more influenced by PFOA surface coverage on the GAC surface in the presence of NOM. Overall, this research contributes valuable insights into pollutant removal strategies, highlighting the potential of DBD plasma-modified GAC in addressing PFOA contamination challenges in water systems. Keywords: Perfluorooctanoic acid (PFOA), dielectric barrier discharge (DBD) plasma, Toth isotherm, Temkin isotherm.

* Corresponding author: Doonyapong.W@chula.ac.th

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1. Introduction

Perfluorooctanoic acid (PFOA), classified as an anthropogenic perfluorinated alkyl substance (PFAS), has gained extensive application as a surfactant in fire retardants, polymer synthesis, paper coatings, and fabric safeguarding. Its distinctive amphiphilic structure encompasses a hydrophilic carboxyl group head and a hydrophobic perfluorinated tail, rendering it versatile [1, 2]. With a substantial C−F bond energy of approximately 440 kJ·mol⁻¹, PFOA exhibits remarkable chemical stability, while its solubility in water (3400 mg·L⁻¹) is facilitated by the presence of the carboxyl group [3, 4]. The implications of PFOA exposure are profound, encompassing adverse health effects such as an elevated risk of kidney and testicular cancer, reproductive toxicity, immunosuppression, and neurological disorders [5, 6]. The urgency to address the environmental and health consequences of PFOA exposure is underscored by its persistent presence in various ecosystems and its connection to serious human health impacts.

Natural organic matter (NOM) constitutes a significant portion of the dissolved organic carbon present in water environments [7]. The way NOM behaves when it interacts with the boundary between solids and water holds crucial significance in various physicochemical processes [8]. For instance, NOM that adheres to surfaces at the water-solid interface can exert a stabilizing effect on colloidal particles [9]. Moreover, this adsorbed NOM can hinder the aggregation and precipitation of these particles [10]. Therefore, gaining insights into the arrangement of NOM at the interface between solids and water becomes imperative to comprehending the specific role of NOM in processes involving the aggregation of colloids and the binding of pollutants.

The plasma treatment process utilizes gases like Ar, He, O₂, N₂, or CO₂ to modify material surfaces, introducing chemical functionalities that bind polymers or other molecules to achieve desired surface properties [11]. Depending on the gas and treatment conditions, effects such as surface activation, abrasion, etching, cross-linking, or a combination can be achieved [12]. Plasma treatment leads to the creation of chemically active species, including hydroxyl, carbonyl, and carboxylic acids, which are generated during plasma treatment, interacting with specific chemical functions on the adsorbent surface [13].

The modification and enhancement of granular activated carbon (GAC) possess the utmost significance in water treatment processes. This study adopted a novel approach to enhance adsorbatibility by employing dielectric discharge plasma (DBD) plasma to modify granular activated carbon (GAC). This technique aims to address the limitations of conventional adsorbents by potentially enhancing their adsorption capabilities. The study investigates the adsorption isotherm behavior using Toth and Temkin isotherm models of PFOA in the presence of NOM, utilizing GAC that has been modified using DBD plasma. There is no literature investigating the adsorption of PFOA and NOM from natural water systems. While experimental PFAS adsorption studies have mainly employed synthetic NOM solutions, natural systems encompass diverse organic compounds. Hence, employing actual water samples is essential for a comprehensive study of adsorption behavior. The Chao Phraya River (CPR), being a major water body in Bangkok, Thailand, is subject to various pollution inputs, such as industrial runoff, agricultural runoff, and urban discharges, all of which can contribute to the diverse composition of NOM present in its water [14]. By selecting CPR as the source of NOM, the study aims to examine the interactions between this complex mixture of organic compounds and the adsorption process under adsorption isotherms investigation.
2. Methodology

2.1 Materials

The CPR sample was taken at lat. 13°54'56.9"N and long. 100°29'38.1"E. and the depth of the river was 3.3 m, the characteristics of CPR water are displayed in Table 1. Subsequently, the water underwent filtration using a pre-washed filter featuring a pore size of 0.3 mm. It was then stored in a refrigerator at a temperature of 4°C. PFOA having a molecular weight of 414.07 g/mol was acquired from Sigma Aldrich. An 85% solution of phosphoric acid (H₃PO₄, PA) was obtained from Anapure. A syringe filter created from glass fibers with a pore size of 2.0 µm was bought from Merck Millipore. Deionized water (DI) was produced in the laboratory and utilized as the standard. Ultra-high purity (UHP) helium and oxygen (O₂) gas cylinders were purchased from Alternative Chemical.

<table>
<thead>
<tr>
<th>pH</th>
<th>TOC (mg/L)</th>
<th>DOC (mg/L)</th>
<th>UV₂₅₄ (cm⁻¹)</th>
<th>SUVA₂₅₄ (L/mg·m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.8</td>
<td>30.153</td>
<td>23.491</td>
<td>0.9572</td>
<td>4.075</td>
</tr>
</tbody>
</table>

2.2 Activated GAC with phosphoric acid (PA)

GAC was soaked in DI water for 4 hours to remove impurities. After thorough washing, the GAC was dried at 50°C for 24 hours. It was then immersed in a 1M solution of phosphoric acid (PA) for 24 hours. After filtration, the GAC was washed with DI water. The filtered residue was dried at 105°C until a constant weight was reached. The resulting PA-activated GAC was used consistently in the entire study.

2.3 DBD plasma treatment of PA-activated GAC

The DBD plasma setup (figure. 1) used an adjustable neon transformer, providing voltages from 0 to 15 kV and a max current of 30 mA. Output power was controlled through a variac linked to the neon transformer. The system featured aluminum parallel-plate electrodes, the discharge electrode (9 cm × 13 cm) and the ground electrode (11 cm × 15 cm). The reaction chamber, an 800 mL borosilicate glass container, was positioned over the ground electrode. A glass dielectric (10 cm × 14 cm) was connected to the discharge electrode. The consistent discharge gap (the space between the glass dielectric's bottom and the reactor's base) was set at 3 mm. During experiments, PA-activated GAC samples underwent DBD plasma treatment. A gas mixture of 30% O₂ and 70% He flowed into the chamber at 1.5 L/min, with independent regulation using mass flow controllers (MFCs). Plasma treatment lasted for 20 minutes and the plasma power was set at 100 W. Afterward, treated GAC samples were sealed in glass containers for subsequent adsorption processes.
2.4 Adsorption experiment

In each batch adsorption, 20 mg of plasma-treated GAC was placed in a glass beaker. Then, 100 mL of a solution containing PFOA, initially at 100 mg/L concentration, was added. Room temperature was maintained during the adsorption, using a magnetic stirrer bar within a glass beaker placed on a hot plate stirrer set at 300 rpm. The process lasted for 24 hours [16]. Gas chromatography-flame ionization detection (GC-FID) was employed to assess the remaining PFOA concentration.

2.4.1 Toth isotherm model

The Toth model (Eq. (1)) was created to enable the Langmuir model to be used in heterogeneous systems [17]. It assumes that the majority of adsorption sites have adsorption energies that are lower than the average energy [18].

\[ q_e = \frac{K_T C_e}{(\alpha_T + C_e^z)^{1/z}} \]  

(1)

where \( K_T \) (mg·g\(^{-1}\)) is the constant, \( \alpha_T \) (mg\(^2\)·L\(^{-1}\)) is the Toth constant, and the parameter \( z \) in the model quantifies the extent of heterogeneity in the adsorption systems, reflecting the degree of variation or diversity in the adsorption sites [18]. \( z \) remains constant and is not affected by changes in temperature, indicating that the degree of heterogeneity in the adsorption systems is independent of the temperature [18]. On the other hand, the value of \( \alpha_T \) increases as the temperature rises, suggesting a temperature-dependent relationship with the adsorption process [19]. When the parameter \( z \) in the Toth model takes a value of 1, the model simplifies to the Langmuir isotherm. However, as the deviation of \( z \) from 1 increases, it indicates a greater level of heterogeneity in the adsorption system.

2.4.2 Temkin isotherm

According to the Temkin model, adsorption occurs via a multi-layer process [20]. The impact of both very high and low adsorbate concentrations in the liquid phase is ignored by this model. In order to incorporate the Temkin isotherm into the Clapeyron-Clausius equation, it was developed a statistical mechanical expression for it [21]. This integration verified that there is a linear decrease in the differential heat of adsorption with increasing coverage.
Eq. 2 represents the Temkin model presented by [20]:

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

(2)

where the constants are denoted by \( A \) (L·g\(^{-1}\)) and \( b \) (J·mol\(^{-1}\)).

3. Results and Discussion

3.1 Toth isotherm model analysis

The Toth isotherm is a mathematical model used to describe the adsorption behavior of solutes onto solid adsorbents [22]. The \( q_{\text{max}} \) of PFOA onto GAC according to the Toth isotherm is 406.42 mg/g for CPR and 229.46 mg/g for DI (Table 2) [15]. The higher \( q_{\text{max}} \) value for CPR suggests that the NOM enhances the adsorption capacity, either by occupying additional adsorption sites or promoting stronger adsorbate-adsorbent interactions. The interactions between PFOA and NOM compounds can enhance the adsorption capacity by facilitating the formation of complexes or promoting cooperative adsorption mechanisms [23].

The adsorption energy (\( K_T \)) of PFOA adsorption onto GAC according to the Toth isotherm is 0.243 L/mg for CPR and 0.237 L/mg for DI. Higher adsorption energy in CPR indicates a stronger affinity between the solute (PFOA) and the adsorbent surface (plasma-treated GAC).

In this case, the higher heterogeneity (\( n \)) value for CPR (0.954) compared to DI (0.648) suggests that the adsorption system in CPR is more heterogeneous in nature. This indicates that there is a wider distribution of adsorption energies on the GAC surface, potentially due to the presence of NOM compounds [23]. The lower value of \( n \) for DI indicates a relatively more homogeneous adsorption system, suggesting more consistent adsorption energy across the GAC surface in the absence of NOM [23].

![Fig. 2. Toth isotherm graph of PFOA adsorption for both DI and CPR.](image-url)
Table 2. Toth isotherm model parameters for PFOA adsorption onto plasma-treated GAC for both DI and CPR samples.

<table>
<thead>
<tr>
<th>Solution</th>
<th>q_{max} (mg/g)</th>
<th>K_T</th>
<th>n</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI</td>
<td>229.46</td>
<td>0.237</td>
<td>0.648</td>
<td>0.994</td>
</tr>
<tr>
<td>CPR</td>
<td>406.42</td>
<td>0.243</td>
<td>0.954</td>
<td>0.992</td>
</tr>
</tbody>
</table>

3.2 Temkin isotherm model analysis

According to the Temkin isotherm (figure. 3), if the adsorption energy drops linearly, which implies that the adsorption process follows a heterogeneous distribution of binding energies [24]. The adsorption intensity parameter (b_T) of the Temkin isotherm, which characterizes the strength of the adsorption process, is determined to be 79.49 for CPR and 78.47 for DI in the case of PFOA adsorption onto plasma-treated GAC (Table 3) [15]. A higher b_T value signified a stronger adsorption interaction between PFOA and GAC, indicating a more favorable and efficient adsorption process. Additionally, the rate of decrease in adsorption energy with increasing surface coverage, as indicated by the b_T values, suggests that the adsorption energy decreases at a slightly faster rate in CPR compared to DI [24]. This implies that the adsorption process in CPR may be more influenced by the surface coverage of PFOA molecules on the plasma-treated GAC surface.

The adsorption capacity parameter (A_T) of the Temkin isotherm, which represents the amount of PFOA that can be adsorbed onto GAC, is determined to be 3.84 for CPR and 1.75 for DI. These values represent the maximum adsorption capacity of PFOA onto GAC according to the Temkin isotherm. The higher A_T value for CPR suggests a greater adsorption capacity compared to DI.

Fig. 3. Temkin isotherm graph of PFOA adsorption for both DI and CPR.
4. Conclusion

This study explored the PFOA adsorption in the presence of NOM using GAC modified with DBD plasma. The need to address PFOA's effects on the environment and human health is urgent due to its amphiphilic nature, widespread usage, and enduring persistence in ecosystems.

The application of Toth and Temkin isotherm models yields valuable insights into the enhanced PFOA adsorption capacity in the presence of NOM using plasma-treated GAC. Based on the $R^2$ values, the Toth isotherm model exhibited better fitting for both DI and CPR water compared to the Temkin isotherm model. The Toth isotherm indicates a higher adsorption capacity ($q_{\text{max}}$) for PFOA in the presence of NOM (CPR), suggesting enhanced adsorbate-adsorbent interactions. The elevated adsorption energy ($K_T$) and heterogeneity ($n$) values in CPR further emphasize NOM's impact on strengthening the affinity between PFOA and GAC.

The Temkin isotherm analysis supports these findings, revealing a stronger adsorption interaction (higher $b_T$) in CPR. The faster decrease in adsorption energy with increasing surface coverage suggests the influence of PFOA surface coverage on GAC in CPR, influencing the adsorption process. The higher adsorption capacity parameter ($A_T$) for CPR highlights its greater adsorption capacity compared to adsorption in DI water.

References

15. T. Sahara, et al. To be published