Kinetics and equilibrium of adsorption of dissolved organic matter fractions from secondary effluent by fly ash

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Abstract
Fly ash was used as a low-cost adsorbent for removing dissolved organic matter (DOM) in secondary effluent. Batch experiments were conducted under various adsorbent dosages, pH, contact time, temperatures and DOM fractional characteristics. Under the optimum conditions of fly ash dosage of 15 g/L, temperature of 303 K and contact time of 180 min, a removal of 22.5% of the dissolved organic carbon (DOC), 23.7% of UV-254, 25.9% of the trihalomethanes precursors in secondary effluent was obtained. The adsorption of DOM fractions onto fly ash all followed the pseudo second-order kinetic model, and the hydrophilic fraction adsorption by fly ash also fitted the intraparticle diffusion model quite well. Freundlich and Langmuir models were applicable to the fly ash adsorption and their constants were evaluated. The maximum adsorption capacities of the adsorptions revealed that fly ash was more effective in adsorbing hydrophilic fraction than the acidic fractions. Structure changes of the DOM fractions after fly ash adsorption were also characterized via spectrum analyzing. Those mechanisms presented critical step toward improved efficiencies of fly ash adsorption via further surface-modification.

Key words: fly ash; adsorption; dissolved organic matter; fractionation; kinetics
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Introduction
Fly ash is a porous solid produced from the combustion of coal in thermoelectric power plants (Cho et al., 2005; Andini et al., 2008). The annual fly ash generation in China is estimated at about 100–120 million tones. Fly ash is a partially developed porous solid waste consisting of SiO₂, Al₂O₃, CaO, and Fe₂O₃ as its major constituents, with varying amounts of unburned carbon (Wang and Wu, 2006; Wang et al., 2008). Although some of fly ash has been applied for road construction, cement production, zeolite synthesis and so on (Estevinho et al., 2007), most of fly ash is dumped without any necessary pretreatment. Thus, making a productive reuse of fly ash is practically urgent, and it may bring considerable environmental benefits.

In the past decades, fly ash has been widely studied in wastewater treatments as a low-cost adsorbent to replace granular activated carbon (GAC) for its low cost, adsorption characteristics and great local availability (Wang and Zhu, 2007). Early works by Kumar et al. (2007) revealed that fly ash was effective in removing phenolic compounds from contaminated wastewater, and Freundlich isotherm was more suitable for simulating the adsorption process. Several studies have shown the overall effectiveness of coal fly ash in adsorbing the humic acid (HA) from aqueous solution, and a higher surface area is beneficial to the adsorption (Wang et al., 2008). Similarly, Wang and Zhu (2007) stated that the content of unburned carbon of fly ash played a major role in HA adsorption. A recent study employing fly ash for a purpose of removing nickel (Ni(II)) and zinc (Zn(II)) from an aqueous solution showed that the effectiveness of fly ash adsorption improved with increasing calcium (CaO) content (Cetin and Pehlivan, 2007). Besides, our previous study for the first time revealed that the additive of fly ash in soil aquifer treatment would significantly enhance the reduction of the dissolved organic matter (DOM) in secondary effluent (Wei et al., 2010). Despite there has been increasing interest in using fly ash as a low cost and easily obtained adsorbent for wastes removal, adsorption mechanism of DOM by fly ash is remain unclear.

DOM in secondary effluent is a heterogeneous mixture of complex aromatic materials that will be converted to carcinogenic disinfection by-products (DBPs) during the chlorination of reclaimed water (Leenheer, 1981; Kim...
and Yu, 2005). Traditionally, tertiary treatment processes such as GAC adsorption, ultrafiltration, reverse osmosis treatment are widely applied to remove those organics (Cheng et al., 2005; Capasso et al., 2005), but the high initial cost and a costly regeneration system make them less economically viable. In such case, the use of low-cost adsorbent of fly ash might be environmentally sensitive. Since the DOM in secondary effluent shows complex polymeric properties, XAD resins fractionation technology is also used for isolation and characterization of those reactive trihalomethanes (THMs) precursors (Leenheer, 1981). Although several studies in the past years have attempted to study the transformation of DOM during the advanced treatments via the using of XAD resin fractionation, to the authors’ knowledge no report has been undertaken to evaluate the effectiveness of fly ash adsorption on DOM fractions. The purposes of this study were to investigate the adsorption capacity of fly ash in removing DOM in secondary effluent under conditions of varied pH, contact time, temperature and fly ash dosage. Moreover, the kinetic characteristics of the adsorption and the changes in chemical composition of the DOM fractions were discussed.

1 Materials and methods

1.1 Materials

The secondary effluent was collected from Taiping Wastewater Treatment Plant (Harbin, China), which employed anaerobic-aerobic activated sludge treatment processes. The raw wastewater received by this plant was mainly municipal wastewater with a small portion of pre-treated industrial wastewater. The collection of secondary effluent performed once a month during the period of March 2010 to June 2010. The averaged water quality of the secondary effluent is summarized in Table 1.

Raw fly ash was obtained from the Harbin No. 3 Thermal Power Plant (China). The main composition of fly ash was found to be SiO₂, 55.7%; Al₂O₃, 25.9%; CaO, 3.7%; Fe₂O₃, 3.3%; K₂O, 2.4%; TiO₂, 0.7%; MgO, 0.3%; Na₂O, 0.2% and loss on ignition (LOI), 5.4%. Its BET specific surface area ranged from 1.3 to 15.6 m²/g, and averaged 2.2 m²/g. The bulk density of the fly ash was around 850–960 kg/m³, comprising the particles with diameter of 0.01–20 μm. The raw fly ash was eluted using Soxhlet extraction method with methanol. Finally, those fly ash was dried at 100°C for 12 hr, cooled, and then stored.

1.2 Fractionation procedure

The DOM within secondary effluent was fractionated using Amberlite XAD resins (Hass, USA) into five fractions: hydrophobic acid (HPO-A), hydrophobic neutral (HPO-N), transphilic acid (TPI-A), transphilic neutral (TPI-N) and hydrophilic fraction (HPI). The detailed description of fraction procedures was given by Wei et al. (2009). To further study the kinetic and thermodynamic characteristics of fly ash adsorption, five DOM fractions were re-diluted with Milli-Q water to produce a dissolved organic carbon (DOC) concentration of 5, 10, 20 and 40 mg/L.

1.3 Adsorption tests

The effect of experimental parameters such as, pH (3–11), initial adsorbent doses (1–30 g/L) and temperature (283–313 K) on the fly ash adsorption was investigated in batch tests. The initial pH of the secondary effluent was adjusted to a desired pH value by adding NaOH or HCl. At the end of adsorption, the suspended fly ash particles were separated using 0.45 μm membrane filter. Specially, the impact of initial fly ash dosages on DOM adsorption was studied at pH 7 and 303 K (stirred at 150 r/min), and the optimum fly ash dosage was 15 g/L. For kinetics studies, the adsorption was studied after adding 15 g fly ash into an aqueous solution containing DOM fractions (5, 10, 20 and 40 mg/L) and shook (150 r/min) at 303 K for various reaction time. Correspondingly, the adsorption isotherms of DOM fractions were studied after adding 15 g of fly ash into the aqueous solution containing a desired DOC concentration (5, 10, 20 and 40 mg/L), and shaking at 150 r/min for 3 hr at different temperatures (283, 293, 303 and 313 K).

1.4 Chlorination

Trihalomethane formation potential (THMFP) analysis was performed for the diluted secondary effluent (1 mg/L) using Standard Method 5710B. All samples were adjusted to pH of 7.0 ± 0.2, buffered with a phosphate solution, and chlorinated with an adequate excess amount of concentrated sodium hypochlorite, ensuring a residual concentration of free chlorine of about 3–5 mg/L at the end of the reaction (requiring 7 days at 25 ± 2°C). Afterwards, the residual chlorine was immediately quenched with sodium sulfate (Na₂SO₃) and the analysis of THMs was conducted immediately. Concentrations of THMs were analyzed by gas chromatograph with an electron capture detector (ECD) (Hewlett Packard 6890 II, USA).

1.5 Analytical methods

All water samples were filtered using 0.45 μm cellulose nitrate membrane filter and stored at 4°C prior to analysis. DOC and UV absorbance was analyzed using Shimadzu TOC-5000 Total Organic Carbon Analyzer and Shimadzu UV-2550 UV/Vis spectrophotometer (Japan), respectively. The instrument was zeroed using Milli-Q water as a blank.

The excitation-emission matrix (EEM) was measured in a 1-cm cuvette using a Jasco FP-6500 spectrofluorometer.

Table 1 Water quality of secondary effluent during experimental period

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean ± SD</th>
<th>Parameter</th>
<th>Mean ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.6 ± 0.2</td>
<td>SS (mg/L)</td>
<td>11.4 ± 2.5</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>49.6 ± 7.4</td>
<td>BOD₅ (mg/L)</td>
<td>13.5 ± 2.7</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>14.4 ± 4.2</td>
<td>Total phosphorus (mg/L)</td>
<td>3.1 ± 1.4</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>12.9 ± 2.4</td>
<td>Chloride (mg/L)</td>
<td>36.2 ± 11.3</td>
</tr>
<tr>
<td>UV-254 (m²/g)</td>
<td>16.3 ± 1.2</td>
<td>NH₄⁺-N (mg/L)</td>
<td>8.2 ± 1.7</td>
</tr>
<tr>
<td>NO₃⁻-N (mg/L)</td>
<td>3.6 ± 1.2</td>
<td>NO₂⁻-N (mg/L)</td>
<td>0.7 ± 0.4</td>
</tr>
</tbody>
</table>
(Japan) at 24°C. Filtered water samples were diluted to 1 mg/L of DOC with 0.01 mol/L KCl, and acidified to pH 3 with HCl. The excitation and emission slits were set to a 5-nm band-pass. Each EEM was generated by scanning excitation wavelengths from 220 to 400 nm with 5 nm step, and detecting the emitted fluorescence between 240 and 480 nm with 1 nm step. The equipment was auto-zeroed prior to each analysis.

The lyophilized powder of 2–5 mg DOM fractions was pressed with 200 mg bromide pellets and measured immediately after preparation under ambient conditions using the Perkin-Elmer Spectrum One B Fourier Transform Infrared (FT-IR) spectrometer (USA). The spectrometer was set to scan from 4000 to 400 cm⁻¹. Spectra were baseline corrected and normalized to 1.0 for the purpose of comparison.

2 Results and discussion

2.1 Effect of initial fly ash dosages on DOM adsorption

The increase in fly ash dosage from 1 to 30 g/L enhanced the removal of DOC, UV-254 and THMFP significantly (Fig. 1), demonstrating that fly ash adsorption would be involved in higher energy sites when the ratios of DOC/fly ash decreased (Kadirvelu and Namasivayam, 2003). The removal of DOC was about 11.3% at 6 g/L fly ash dosage and was 22.5% at 15 g/L fly ash dosage, which reached to 27.0% when the fly ash dosage increased to 30 g/L. Based on the above-mentioned results (Fig. 1), an fly ash dosage of 15 g/L was chosen. Removal trends of the aromatic components and THMs precursors (23.3% and 25.9% removal at 15 g/L fly ash dosage, respectively) were similar to that of DOC (Fig. 1). Since only 34.9% of the aromatic components in secondary effluent could be adsorbed by GAC (dosage of 1 g/L) (Wei et al., 2008), fly ash was attractive as a potential low-cost adsorbent than GAC in removing DOM from secondary effluent. In addition, an increase of fly ash dosage would enhance the adsorption of THMs precursors and lead to a decreased specific THMFP of the post-fly ash effluent.

How to dispose those used fly ash might be practically urgent. Because the amount of DOM adsorbed on fly ash was quite low (about 0.2 mg/g at the fly ash dosage of 15 g/L), the used fly ash could be applied for concrete production (Poon et al., 2000; McCarthy and Dhir, 2005). Since the sintering temperature of combustion was set above 1200°C, the organics adsorbed on fly ash would be converted to harmless CO₂ (Adell et al., 2007, 2008).

2.2 Effect of pH and temperature on DOM adsorption

The adsorption of the aromatic DOM in secondary effluent on fly ash as a function of hydrogen ion concentration was examined over a pH range of 3–11 (Fig. 2a). After a 3 hr adsorption at 303 K (15 g/L fly ash dosage), more UV-254 could be removed under higher pH, which was inconsistent with the results obtained by Wang and Zhu (2007) who stated that the adsorption of humic acid on fly ash decreased when the solution pH was increased. This was ascribed that the increase of negatively charged sites on fly ash at a high pH value would lead to an effective adsorption of the positively charged pollutants (Bousher et al., 1997), and those polymeric components could flocculate the aromatic materials efficiently. Similarly, THMs precursors in secondary effluent could be also preferentially adsorbed under alkaline condition (data not given).

As shown in Fig. 2b, the optimum temperature for DOM removal was found to be 303 K, at which maximum UV-254 reduction of 23.7% was observed (pH 7). In the case of 283, 293 and 313 K, UV-254 removal efficiency was 19.6%, 23.3% and 23.5%, respectively. In addition, fly ash adsorption at higher temperature condition needed a longer time to reach equilibrium state.

![Fig. 1](Image) Effect of initial fly ash dosages on DOC, UV-254 and trihalomethane formation potential (THMFP) reduction of the secondary effluent.

![Fig. 2](Image) Effect of pH (a) and temperature (b) on UV-254 reduction of the secondary effluent during fly ash adsorption.
2.3 Effect of characteristic of DOM fractions on fly ash adsorption

To evaluate the thermodynamic and kinetic characteristics of organics adsorption on fly ash, the solutions of five DOM fractions were prepared in low DOC concentrations (5, 10, 20 and 40 mg/L). As shown in Fig. 3, an increase of the contact time from 0.0 to 1.0 hr enhanced the removal of DOM fractions significantly. Adsorption kinetics of the DOM fractions by fly ash could be described by pseudo first-order Lagergren equation, pseudo second-order rate equation and the intraparticle diffusion model (Ho and Chiang, 2001; Wang et al., 2008), which can be expressed in linear forms as Eqs. (1), (2) and (3), respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$  \hspace{1cm} (1)

$$\frac{t}{q_t} = \frac{1}{q_e k_2} + \frac{t}{q_e}$$  \hspace{1cm} (2)

$$q_t = k_i (t^{1/2}) + C$$  \hspace{1cm} (3)

where, \(k_1\) (min\(^{-1}\)), \(k_2\) (g/(mg-min)) and \(k_i\) (g/(mg-min\(^{0.5}\))) are the rate constants of pseudo first-order adsorption, pseudo second-order adsorption and the intraparticle diffusion, respectively. \(C\) (mg/g) is the intercept, \(q_e\) (mg/g) and \(q_t\) (mg/g) are amount of DOM fractions adsorbed on adsorbent at equilibrium and at time \(t\), respectively.

As shown in Table 2, the second-order kinetic model yielded a much better fit than the other two models in simulating the adsorption processes of all five DOM fractions \((R^2 > 0.9899)\). In overall, fly ash was more efficient in adsorbing the hydrophilic and neutral components, as evidenced by the decreased \(k_2\) value of HPI (0.271 g/(mg-min)) > TPI-N (0.242 g/(mg-min)) > HPO-N (0.228 g/(mg-min)) > HPO-A (0.176 g/(mg-min)) > TPI-A (0.120 g/(mg-min)). The adsorption of HPI reached equilibrium slowly (>150 min), and could also be described by the intraparticle diffusion model \((R^2 = 0.9760)\), ascribing to the intraparticle adsorption of low molecular-weight HPI in micropores (Quanrud et al., 2004). On contrast, HPO-A showed a rapid adsorption fitting the first-order kinetic

![Fig. 3 Effect of initial DOC concentration of fractional DOM on fly ash adsorption. HPO-A: hydrophobic acid; HPO-N: hydrophobic neutral; TPI-A: transphilic acid; TPI-N: transphilic neutral; HPI: hydrophilic fraction.](image-url)

Table 2  Kinetic parameters of DOM and its fractions for fly ash adsorption at 303 K

<table>
<thead>
<tr>
<th></th>
<th>C(_0) (mg/L)</th>
<th>(q_e) (mg/g)</th>
<th>(k_1) (min(^{-1}))</th>
<th>(R^2)</th>
<th>(q_e) (mg/g)</th>
<th>(k_2) (g/(mg-min))</th>
<th>(R^2)</th>
<th>(k_i) (g/(mg-min(^{0.5})))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOM</td>
<td>10</td>
<td>0.136</td>
<td>0.0228</td>
<td>0.8915</td>
<td>0.144</td>
<td>0.462</td>
<td>0.9899</td>
<td>0.0045</td>
<td>0.9287</td>
</tr>
<tr>
<td>HPO-A</td>
<td>10</td>
<td>0.173</td>
<td>0.0189</td>
<td>0.9518</td>
<td>0.176</td>
<td>1.171</td>
<td>0.9993</td>
<td>0.0026</td>
<td>0.9015</td>
</tr>
<tr>
<td>TPI-A</td>
<td>10</td>
<td>0.122</td>
<td>0.0117</td>
<td>0.6293</td>
<td>0.120</td>
<td>1.326</td>
<td>0.9932</td>
<td>0.0018</td>
<td>0.6284</td>
</tr>
<tr>
<td>HPO-N</td>
<td>10</td>
<td>0.236</td>
<td>0.0085</td>
<td>0.8770</td>
<td>0.228</td>
<td>0.259</td>
<td>0.9967</td>
<td>0.0098</td>
<td>0.7750</td>
</tr>
<tr>
<td>TPI-N</td>
<td>10</td>
<td>0.242</td>
<td>0.0127</td>
<td>0.9047</td>
<td>0.242</td>
<td>0.458</td>
<td>0.9983</td>
<td>0.0071</td>
<td>0.9019</td>
</tr>
<tr>
<td>HPI</td>
<td>10</td>
<td>0.259</td>
<td>0.0164</td>
<td>0.9227</td>
<td>0.271</td>
<td>0.213</td>
<td>0.9932</td>
<td>0.0102</td>
<td>0.9760</td>
</tr>
</tbody>
</table>
model ($R^2 = 0.9518$).

### 2.4 Adsorption isotherms

To successfully represent the thermodynamic adsorptive behaviors of fly ash, Langmuir and Freundlich isotherms were employed to describe the sorption process of DOM fractions (Wang et al., 2008; Wang and Zhu, 2007). The Langmuir isotherm and Freundlich isotherm can be described by Eqs. (4) and (5), respectively:

\[
\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \quad (4)
\]

\[
\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)
\]

where, $q_e$ (mg/g) is the amount adsorbed, $C_e$ (mg/L) is the equilibrium concentration of the adsorbate, $Q_0$ and $b$ are Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. $K_F$ (mg/g) and $n$ are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.

The values of $Q_0$, $b$, $K_F$, $n$, and the linear regression correlations for the Langmuir and Freundlich isotherms are given in Table 3. Because the Langmuir regression coefficients ($R^2$) of HPO-A, TPI-A and TPI-N (0.9864, 0.9945 and 0.9996, respectively) were much higher than the corresponding $R^2$ of Freundlich isotherm (0.9613, 0.9768 and 0.9690, respectively), it appeared that the monolayer adsorption process of Langmuir model yielded a much better fit than the Freundlich model in simulating the adsorption of these three fractions. On the other hand, the Freundlich model was more suitable for simulating the adsorption of HPO-N and HPI. The maximum adsorption capacities of the DOM fractions (Table 3) showed TPI-N (0.515) > HPI (0.463) > HPO-N (0.344) = HPO-A (0.344) > TPI-A (0.178).

The effect of temperature on adsorption of DOM fractions was studied for the temperature range of 283–313 K. The results are summarized in Table 4. The Gibb's free energy ($\Delta G^0$), enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) for the adsorption process were obtained using the following equations:

\[
\Delta G^0 = -RT \ln K_C \quad (6)
\]

\[
\ln \left( \frac{K_{C2}}{K_{C1}} \right) = \left( \frac{\Delta H^0}{R} \right) \left( \frac{T_2 - T_1}{T_1T_2} \right) \quad (7)
\]

\[
\ln K_C = \frac{\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)
\]

where, $K_C$, $K_{C1}$ and $K_{C2}$ are the equilibrium constant (ratio of the equilibrium concentrations of DOM fractions on the adsorbent and in the solution) of the adsorption process at temperature $T$, $T_1$ and $T_2$, $R$ and $T$ are gas constant and absolute temperature, respectively. $\Delta G^0$, $\Delta S^0$ and $\Delta H^0$ can be calculated from a plot of $\ln K_C$ versus $1/T$.

The calculated $\Delta H^0$ and $\Delta S^0$ values for the adsorption of DOM in secondary effluent are 7.43 kJ/mol and 48.45 kJ/(mol·K), respectively. The positive $\Delta H^0$ value and negative $\Delta G^0$ value of the DOM fractions suggested the endothermic and spontaneous nature of fly ash adsorption (especially for HPI). Specially, the relatively higher $\Delta H^0$ and $\Delta S^0$ value of HPI (10.45 kJ/mol and 64.43 kJ/(mol·K), respectively) might be the main reason for its highest removal efficiency during fly ash adsorption. In addition, the value of $R^2$ for all DOM fractions was much higher than that of secondary effluent, ascribing to the simpler chemical characteristics of DOM fractions in comparison with the unfraccionated DOM.

### 2.5 Characteristics and behaviors of DOM fractions during fly ash adsorption

#### 2.5.1 EEM spectra

The EEM spectra of five DOM fractions in secondary effluent revealed significant fluorescence peaks in Regions II and III, and regime V by Chen et al. (2003), referring to the redundancy of aromatic tryptophan-like proteins, fulvic-like and humic-like materials, especially for the acidic fractions (Fig. 4). Moreover, the neutral fractions (HPO-N and TPI-N) also showed shoulder peaks of SMP-like components (regime IV). The fluorescent intensity of Region II and V of secondary effluent decreased 33.3% and 27.7%.

### Table 3 Parameters of Langmuir and Freundlich isotherms for fly ash adsorption at 303 K

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$Q_0$ (mg/g)</td>
<td>$b$</td>
</tr>
<tr>
<td>HPO-A</td>
<td>0.344</td>
<td>0.3406</td>
</tr>
<tr>
<td>TPI-A</td>
<td>0.178</td>
<td>0.6572</td>
</tr>
<tr>
<td>HPO-N</td>
<td>0.344</td>
<td>0.3401</td>
</tr>
<tr>
<td>TPI-N</td>
<td>0.515</td>
<td>0.2272</td>
</tr>
<tr>
<td>HPI</td>
<td>0.463</td>
<td>0.2529</td>
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</table>

### Table 4 Thermodynamic parameters for fly ash adsorption

<table>
<thead>
<tr>
<th></th>
<th>$\Delta G^0$ (kJ/mol)</th>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (kJ/(mol·K))</th>
<th>$R^2$</th>
</tr>
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<tbody>
<tr>
<td>283 K</td>
<td>7.43</td>
<td>8.31</td>
<td>52.91</td>
<td>0.7290</td>
</tr>
<tr>
<td>293 K</td>
<td>7.43</td>
<td>8.31</td>
<td>52.91</td>
<td>0.7290</td>
</tr>
<tr>
<td>303 K</td>
<td>7.43</td>
<td>8.31</td>
<td>52.91</td>
<td>0.7290</td>
</tr>
<tr>
<td>313 K</td>
<td>7.43</td>
<td>8.31</td>
<td>52.91</td>
<td>0.7290</td>
</tr>
</tbody>
</table>
Fig. 4  EEM of DOM fractions before and after fly ash adsorption at 15 g fly ash dosage, 303 K, pH 7 and initial fractional DOC concentration of 10 mg/L.
when the fly ash adsorption progressed (at initial DOC of 10 mg/L), indicating those tryptophan-like proteins and aromatic fulvic-like materials were efficiently adsorbed. On the other hand, the removal efficiency of the humic-like and SMP-like components was quite low. Overall, fly ash tended to adsorb the hydrophobic related fulvic-like materials preferentially (45.0% for HPO-A and 54.3% for HPO-N), followed by the transphilic fractions (41.8% for TPI-N and 32.3% for TPI-A), while that of HPI was the lowest. Correspondingly, the removal efficiency of the humic-like materials (Region V) showed a decreased trend of HPO-N (57.1%) > TPI-N (49.3%) > TPI-A (43.7%) > HPO-A (39.7%) > HPI (34.9%). Yang et al. (2008) commented that the activated aromatic sites, especially those polyhydroxy aromatic moieties and aromatic β-Diketones (humic-like and fulvic-like related), played an important role in the formation of THMs during chlorination. Thus, the efficient adsorption of those two fluorophores might be the main reason for the decreased specific THMFP of the fly ash adsorbed effluent. Fluorophores of TPI-N and HPI in Regions IV showed a significant intensity decrease when the fly ash adsorption progressed, implying the preferential adsorption of the small molecular in SMP-like materials.

2.5.2 FT-IR spectra

FT-IR spectra for the DOM fractions before and after fly ash adsorption are shown in Fig. 5. Most of the observed peaks correlated with those reported in Wei et al. (2010) that the aromatic C=C and carboxylic C=O compounds were the substances readily adsorbed during fly ash adsorption. The noticeable absorbance band at 1718 cm⁻¹ for acidic fractions in secondary effluent was assigned to be C=O stretching of carboxylic acids, aldehydes, ketones and esters, indicating the presence of carboxylic acids in those two acidic fractions. The aromatic C=C (1650–1550 cm⁻¹) related components were only observed in fractions HPO-A, HPO-N, TPI-A and TPI-N as a shoulder peak. Moreover, strong signals at 1420 cm⁻¹ and 1250–1000 cm⁻¹ in neutral and hydrophilic fractions of secondary effluent were consistent with the character of those three fractions, corresponding to aliphatic groups of intermediate polarity and low molecular weights (Chen et al., 2002).

Following the fly ash adsorption at an initial concentration of 10 mg/L, the hydrocarbon peaks (1250–1050 cm⁻¹) were reduced for all DOM fractions (except HPI), indicating that the hydrocarbons were effectively adsorbed. This trend was more apparent in neutralic fractions than in acidic fractions. The intensities of the carboxylic C=O
peaks (1720–1690 cm\(^{-1}\)) decreased significantly for the acidic fractions, but slightly increased for the neutral and hydrophilic fractions, indicating that the fly ash yielded a better adsorption of those carboxylic macromolecule in acidic fractions. Contrarily, the fly ash adsorption eliminated the aromatic C=C (1550 cm\(^{-1}\)) and aliphatic C–H (1420 cm\(^{-1}\)) components in neutral and hydrophilic fractions, while that of the acidic fractions increased. In addition, the intensities of neutral fractions related aromatic C–H peaks while that of the acidic fractions increased. In addition, the intensities of neutral fractions related aromatic C–H peaks while that of the acidic fractions increased.

3 Conclusions

Based on the experimental results, the conclusions can be drawn as follows:

Removal efficiencies of 22.5% for DOC, 23.7% for UV-254, 25.9% for THMs precursors were observed for the secondary effluent during fly ash adsorption under the optimum conditions (15 g/L fly ash dosage, 303 K, pH 7 and 180 min contact time).

The second-order kinetics yielded a much better fit (\(R^2 > 0.9899\)) for simulating the fly ash adsorption of all DOM fractions, and the pseudo second-order rate constants (g/(mg-min)) decreased in trend of HPI (0.271) > TPI-N (0.242) > HPO-N (0.228) > HPO-A (0.176) > TPI-A (0.120). Moreover, the adsorption of HPI by fly ash could be also molded by intraparticle diffusion model (\(R^2 = 0.9760\)), and that of HPO-A was fitted to the first-order kinetic model as well (\(R^2 = 0.9518\)). Overall, HPO-A showed a rapid adsorption while that of HPI reached equilibrium slowly. Langmuir isotherm could well simulate the fly ash adsorption of HPO-A, TPI-A and TPI-N (\(R^2 = 0.9864, 0.9945\) and 0.9996, respectively), while Freundlich model yielded a much better fit in simulating the adsorption of HPO-N and HPI. The positive \(\Delta H^0\) value and negative \(\Delta G^0\) value of the DOM fractions suggested the endothermic and spontaneous nature of fly ash adsorption (especially for HPI).

The C=O related carboxylic (fulvic-like and fulvic-like) components in acidic fractions could be more readily adsorbed by fly ash in comparison with that of the aliphatic materials and hydrocarbon. Meanwhile, fly ash was accessible to adsorb the protein-like and SMP-like materials in neutral fractions and HPI (hydrocarbons and amide II related) preferentially.

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