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Removal and transformation of organic matters in domestic wastewater during lab-scale chemically enhanced primary treatment and a trickling filter treatment

Qingliang Zhao^{1,*}, Huiyuan Zhong¹, Kun Wang¹,
Liangliang Wei¹, Jinli Liu¹, Yu Liu²

1. State Key Laboratory of Urban Water Resources and Environments, School of Municipal and Environmental Engineering,
Harbin Institute of Technology, Harbin 150090, China

2. School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

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Abstract

To find a simple and economical way for treating the domestic wastewater in small counties and towns, a process combining chemically enhanced primary treatment and a trickling filter (CEPT-TF, representing the physical and biological effects) was constructed and operated in laboratory conditions. The characteristic behaviors of dissolved organic matter in raw wastewater and effluents were examined during steady-state operation. Experimental results showed that the process of CEPT and TF in series was beneficial for the removal of hydrophobic and hydrophilic organics. Specially, the hydrophobic and aromatic materials could be preferentially removed in the CEPT unit, and the hydrophilic fraction in the TF. Structural changes of the organic fractions during the operation of the different units were also characterized via spectrum analysis.

Key words: dissolved organic matter; fractionation; fly ash; coal cinder; coagulation; biodegradation

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Introduction

Centralized sewage treatment plants need collection and/or transportation of domestic wastewater and are generally not suitable for towns and villages where the residents are scattered (Netter et al., 1994). Since the direct discharge of domestic wastewater is responsible for a high risk of infectious disease transmission (Hinckley et al., 2008; Guizani et al., 2011), how to safely and effectively treat these wastewaters in a practical manner is an urgent question. In China, small towns mainly refer to entities between a city and rural village, characterized by a certain scale, and mainly engaged in non-agricultural activities. They also include an administrative department, a regional center for the economy, culture and life service, with an ideal size for population below 20000. They are characterized by huge numbers, small scale and wide distribution (Qiao and Wang, 2003). To the author's knowledge, there are still more than 550 counties and 15000 towns in China where there are no wastewater treatment plants, and the majority of the wastewater in these regions needs to be treated in

the coming five years. Therefore, finding a simple and economical process is meaningful and will help us in designing a wastewater treatment plant for counties and small towns.

Dissolved organic matter (DOM) in wastewater is a complex mixture of aromatic and aliphatic hydrocarbon structures that have attached amide, carboxyl, hydroxyl, ketone, and various minor functional groups. DOM can include infection by pathogens to give rise to health concerns (Drewes and Fox, 1999; Kanokkantapong et al., 2006b), especially for these small counties and towns. It has also been highly concerning that DOM could be converted to carcinogenic disinfection by-products (DBPs) during chlorination. Therefore, attention to the transformation of the DOM during sewage treatment should be given a high priority (Guo et al., 2011). Because of its complex polymeric properties, XAD resin fractionation technology has been widely applied for measuring the characteristics of DOM when evaluating the environmental behavior of these organic contaminants (Leenheer and Croue, 2003; Chaminda et al., 2010).

The main processes responsible for DOM removal

* Corresponding author. E-mail: qlzhao@hit.edu.cn

during sewage treatments have been characterized as aerobic/anaerobic biodegradation and coagulation. Specifically, the biodegradation process is inclined to remove the hydrophilic DOM preferentially (Wei et al., 2012), whereas the hydrophobic components tend to be preferentially removed during the flocculation and anaerobic biodegradation processes (Xu et al., 2011). Activated sludge processes have been recognized as the most powerful technology being widely applied in industrial and municipal wastewater treatment plants, but these techniques are too complex, costly, and time consuming for small towns. Thus, to find an inexpensive, environmentally friendly approach for DOM removal which is suitable for small towns is practically urgent.

Coagulation is frequently used for organics removal during wastewater treatment (Wang et al., 2010), especially for macromolecular-related hydrophobic DOM (Xu et al., 2011). Polyaluminum chloride and polyferric chloride have been traditionally used in wastewater and drinking water treatment. In addition, fly ash has recently been applied as an alternative material for preparing wastewater coagulant, in which the aluminum and iron oxides are the active portions during the chemically enhanced primary treatment (CEPT) (Fan et al., 2002). It should be pointed out that the CEPT process could only remove part of the COD, but was less efficient for $\text{NH}_4^+\text{-N}$ removal (Liu et al., 2009). By comparison, the DOM in wastewater could be efficiently utilized by the biomass in the trickling filter (TF) (Guo et al., 2011), leading to a reduction of biodegradable organics and $\text{NH}_4^+\text{-N}$. Because of its easy operation, great tolerance of hydraulic loading, and no requirement of aeration (Tekerekopoulou and Vayenas, 2003), the TF process has been recognized as a powerful technology for removing organics and $\text{NH}_4^+\text{-N}$, especially in small counties and towns (Barker and Stuckey, 1999). Based on the analyses mentioned above, the systems of CEPT and TF could be theoretically combined in series for removal of DOM and $\text{NH}_4^+\text{-N}$ in sewage wastewater, which can efficiently remove these DBPs precursors. In order to guide the operation of CEPT-TF systems, the characteristic behavior of DOM during treatment needs to be further examined in depth.

The objective of this study was to differentiate the removal mechanisms of DOM during a lab-scale CEPT-TF operation. Specific objectives included: (1) identifying the characteristics and transformation of DOM within each process of the CEPT-TF system; (2) evaluating the effect of CEPT-TF operation on the molecular weight distribution of DOM fractions, and (3) examining the impacts of the CEPT-TF on the chemical compositions of the influent DOM.

1 Materials and methods

1.1 Characteristics of the wastewater and materials

Experimental domestic wastewater was obtained from the residential areas near the Harbin Institute of Technology. The parameters of average temperature, chemical oxygen demand (COD), $\text{NH}_4^+\text{-N}$, suspended solids (SS), total phosphorous (TP) and pH were determined according to standard methods (China EPA, 2002).

The raw fly ash was obtained from the Harbin No.3 Thermal Power Station in Heilongjiang Province, China. The main compositions of the fly ash were determined by X-ray fluorescence (XRF) testing, which found it to contain SiO_2 55.7%, Al_2O_3 20.9%, CaO 3.7%, MgO 0.3%, Fe_2O_3 3.3%, K_2O 2.4% and Na_2O 0.2%. The loss on ignition (LOI) was 13.5%. The specific surface area of the fly ash ranged from 1.25 to 1.61 m^2/g as determined by the Brunauer-Emmett-Teller nitrogen adsorption technique. A high percentage of the fly ash consisted of particles with diameter 0.01–20 μm and the bulk density of the fly ash adsorbent was 850–960 kg/m^3 .

Coal cinder was obtained from the boiler room at Harbin Institute of Technology, China. The coal cinder contained SiO_2 55.0%, Al_2O_3 26.9%, Fe_2O_3 4.3%, K_2O 2.0%, CaO 1.7%, MgO 0.5%, Na_2O 0.6% and LOI 9.0% as determined by XRF testing. The specific surface area of the coal cinder ranged from 0.45 to 0.61 m^2/g (averaged 8 mm diameter), determined by the Brunauer-Emmett-Teller nitrogen adsorption technique.

1.2 CEPT-TF system description

The process of the CEPT-TF system, as shown in Fig. 1, was comprised of two individual units of CEPT and TF. Specifically, a mixing zone (50 × 50 × 50 mm), three reaction zones (50 × 50 × 100 mm) and an inclined-plate settling tank (100 × 100 × 150 mm) formed the CEPT unit. In addition, the stirring intensities for the mixing and three reaction zones were 150, 70, 60 and 40 r/min, respectively. The influent flow of the CEPT was set to 40 L/day, corresponding to a theoretical hydraulic retention time (HRT) of 30 min.

Fig. 1 Schematic of the CEPT-TF system.

Fly ash was explored as a raw material for the production of a complex coagulant by treatment with a sulfuric acid solution at 120°C for 4 hr according to a previous study (Fan et al., 2005). It was found the optimum fly ash coagulant dosage was 2.5 mL/L (Zhao et al., 2012). The fly ash coagulant was diluted 50 times and introduced into the reaction zone of the CEPT unit by a peristaltic pump. The CEPT effluent samples were collected under steady state after water was sedimented in the inclined-plate settling tank.

Coal cinder (about 8 mm in diameter), which consisted of iron oxide with low particle size and high surface area (Parks, 1965; Music and Ristic, 1992), was applied as the packing medium of the TF columns. The TF unit was 0.08 m in internal diameter and 2.4 m in height, and was separated into four uniform parts in order to enhance the natural ventilation for sufficient oxygen supply. Sludge from the secondary sedimentation tank of a wastewater treatment plant was applied to establish the biofilm in the TF unit (Haseborg et al., 2010). The effluent from the CEPT (40 L/day) was pumped into the TF unit using a sprayer which was located at the top of the TF column, with a fixed hydraulic loading rate of 1.5 kg COD/(m²·day).

1.3 Fractionation procedure

DOM was fractionated by Amberlite XAD-8/XAD-4 resins into five fractions: hydrophobic acid (HPO-A), hydrophobic neutral (HPO-N), transphilic acid (TPI-A), transphilic neutral (TPI-N) and hydrophilic fraction (HPI). The domestic wastewater samples were filtered (by 0.45 µm filter) and acidified (pH 2), and then passed through two columns in series containing XAD-8 and XAD-4 resins. HPO-A and TPI-A were eluted from the XAD-8 and XAD-4 columns, respectively, using 0.1 mol/L NaOH. HPO-N and TPI-N were the compounds that adsorbed onto the XAD-8 and XAD-4 resins, respectively, but were not dissolved during back elution with NaOH. HPI was the carbon not retained on either resin. A complete description of the isolation methods was given by Wei et al. (2009).

1.4 Analytical methods

All water samples were collected and analyzed immediately after the reactor achieved steady-state operation. The samples were collected daily and stored at 4°C until they were analyzed. The DOC and UV-254 was analyzed by a Shimadzu TOC-5000A Organic Carbon Analyzer (Shimadzu, Kyoto, Japan) and Shimadzu UV-2550 ultraviolet-visible spectrophotometer (Shimadzu, Kyoto, Japan), respectively. Specific ultraviolet light absorbance (SUVA) was calculated as (UV-254/DOC)×100.

The molecular weight of the DOM fraction was characterized by liquid high performance size exclusion chromatography (HPSEC) (LC-10A, Shimadzu, Japan) with UV-detection (SPD-10A) at 254 nm. The mobile phases were composed of Milli-Q water buffered to pH

6.8 with 0.1 mol/L NaCl, 0.002 mol/L phosphate buffer and the flow rate was set at 0.4 mL/min (Kwon et al., 2005). The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) were calculated from the HPSEC-UV results using polyethylene glycol (0.6, 1, 6, 20 kDa) as molecular weight standards (Bu et al., 2010). Polydispersity (d) was calculated with the following equation:

$$d = M_w/M_n$$

Fluorescence spectra were measured in a 1-cm quartz cell using a Jasco FP-6500 spectrofluorometer at the ambient temperature of 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 to minimize complexation of metals with DOC (Drewes et al., 2006). The excitation and emission slits were set to a 5 nm band-pass and scan speed was set at 1000 nm/min. A blank sample consisting of 0.01 mol/L KCl at pH 3 was also measured in the 1-cm path length quartz cell.

The infrared spectra of HPO-A, HPO-N, TPI-A, TPI-N were obtained using 2–5 mg of powder lyophilized in potassium bromide pellets. The Perkin-Elmer Spectrum One B Fourier Transform Infrared (FT-IR) spectrometer was set to scan from 4000 to 400 cm⁻¹. Spectra were baseline corrected and normalized to 1.0 for purposes of comparison.

2 Results and discussion

2.1 Water quality of the CEPT-TF effluent

Following an acclimation period of approximately 2 months, the average removal efficiency of COD, NH₄⁺-N, TP and SS of the CEPT-TF system was 91%, 82%, 100% and 98%, respectively (Table 1). Notably, the majority of NH₄⁺-N (78%) was removed within the TF unit, while 89% of the TP reduction was attributed to the CEPT operation. The above results demonstrated that the nitrification and denitrification by microorganisms in TF unit played an important role in NH₄⁺-N removal. In contrast, the majority of the TP was removed by coagulation and adsorption in the CEPT unit. The maximum adsorption capacity of coal cinder is 0.398 mg P/g (Yang et al., 2009), which is smaller than other adsorbents. Zhao et al. (2012) showed the most TP removal in the TF unit happened after the biofilm was built, which meant the major removal mechanism of TP in the TF unit was microbial action. The

Table 1 Wastewater quality during domestic wastewater treatment

Parameter	Raw wastewater	Effluent of CEPT	Effluent of TF
COD (mg/L)	328 ± 25	177 ± 14	28 ± 5.6
NH ₄ ⁺ -N (mg/L)	35.2 ± 5.8	29 ± 4.6	6.5 ± 1.2
TP (mg/L)	4.9 ± 0.8	0.6 ± 0.1	0.05 ± 0.01
SS (mg/L)	211 ± 55	20 ± 6	4.5 ± 2.3

Fig. 2 Removals of COD, DOC and UV-254 during CEPT-TF treatment.

coagulation mechanism in the CEPT produced the same level of COD reduction as the aerobic biodegradation in the TF. Thus, the design configuration of CEPT and TF in series could make use of the functions of both coagulation in the CEPT and biodegradation within the TF, which could lead to an increased removal of TP and $\text{NH}_4^+\text{-N}$, and would be beneficial for the sewage wastewater treatment of small towns.

The removals of COD, DOC and UV-254 during CEPT-TF treatment are summarized in **Fig. 2**. A total average reduction of COD (91%), DOC (77%), and UV-254 (48%) could be achieved after the domestic wastewater was treated by the CEPT-TF system. When the CEPT-TF system progressed, the water quality of the effluent could achieve the level IB of the Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant (GB 18918-2002), which has been reported previously (Zhao et al., 2012).

2.2 Changes of DOC composition at different treatment stages

An average of 76.9% of the DOC of the influent was removed as a consequence of CEPT-TF operation (decreased from 59.5 to 13.7 mg/L), of which the TF unit showed much higher DOC reduction than that of the CEPT (54.2% vs. 22.7%). These results indicated that the aerobic/anaerobic biodegradation in the TF unit played a key role in the DOM reduction during the CEPT-TF operation. HPI was the predominant fraction in the raw wastewater (**Fig. 3**), accounting for 57.5% of total DOM, followed by HPO-A (20.7%) and TPI-A (11.4%), whereas the neutral fractions were quite low (6.7% for HPO-N and 3.7% for TPI-N). Both of the predominant fractions of HPO-A and HPI were efficiently removed during the CEPT-TF operation (77.7% for HPO-A and 79.3% for HPI), implying that the coagulation and biodegradation functioned well. It is noteworthy that TPI-N showed the lowest DOC reduction of 46.6% during the CEPT-TF process.

The polarity distributions of influent DOM changed

Fig. 3 DOC concentrations for DOM and its fractions in the raw domestic wastewater and the effluents of the CEPT and TF units. HPO-A: hydrophobic acid; HPO-N: hydrophobic neutral; TPI-A: transphilic acid; TPI-N: transphilic neutral; HPI: hydrophilic fraction.

significantly during the CEPT-TF treatment. As shown in **Fig. 3**, the acidic and hydrophobic fractions of influent DOM could be preferentially removed by the CEPT unit (26.8%, 26.8% and 32.5% for HPO-A, HPO-N and TPI-A, respectively), whereas that of HPI was much lower (19.2%). In the subsequent TF unit, the DOC removal efficiency of the five fractions showed a decreasing trend of HPI (60.1%) > HPO-A (50.9%) > TPI-A (45.9%) > HPO-N (42.9%) > HPI (25.4%). The fact that HPI experienced the highest DOC reduction in the TF unit was mainly ascribed to its biodegradable characteristics. For comparison, the efficient removal of the hydrophobic and acidic fraction was attributed to the optimum layout of sorption and aerobic/anaerobic biodegradation in the CEPT-TF system.

It has been demonstrated that the HPI fractions could be preferentially utilized by biomass due to its biodegradable characteristics (Bu et al., 2010), while HPO-A could be more efficiently coagulated instead. Thus, the design configuration of the CEPT and TF is efficient for the removal of these two dominant organic fractions regardless of their chemical characteristics. The DOM in the CEPT-TF effluent became more hydrophobic, which could be demonstrated by the decreased content of HPI (from 57.5% to 51.9%) and the increased content of hydrophobic fractions, implying that the biodegradation mechanism predominated in the CEPT-TF unit over that of coagulation.

2.3 Molecular weight changes of DOM after CEPT-TF treatments

The apparent M_w distribution of DOM in two different effluents was measured by HPSEC and given in terms of UV absorbance at 254 nm (**Table 2**). The M_w of the influent DOM decreased significantly when the CEPT operation progressed (from 462108 to 291167 Da), which can be ascribed to the significant coagulation of the macromolecules in DOM by the fly ash coagulant (Pallier et al., 2011). For comparison, a subsequent decrease of M_w

Table 2 Molecular weight and polydispersity of DOM fractions in the domestic wastewater and effluent samples from the CEPT-TF system in series

Sample fraction	M_w (Da)	M_n (Da)	d
Raw domestic water	462108	2183	211
HPO-A	961238	831	1157
TPI-A	56729	451	126
HPO-N	125869	522	241
TPI-N	85949	391	219
HPI	1047	290	3.6
Effluent of CEPT	291167	1754	166
HPO-A	207214	2332	89
TPI-A	47108	655	72
HPO-N	60223	271	222
TPI-N	43711	253	172
HPI	3062	870	3.5
Effluent of TF	54821	1992	28
HPO-A	34034	1005	34
TPI-A	4289	1125	3.8
HPO-N	3081	407	7.6
TPI-N	737	181	4.1
HPI	1294	318	4.0

for the TF effluent (from 291167 to 54821 Da) further indicated that the high molecular related organics were aerobic/anaerobically destroyed.

As indicated in **Table 2**, the fractional M_w value of the organics for the raw wastewater ranged from 1047 to 961238 Da, in which the highest M_w value of HPO-A was attributed to its least polarity and highest polymeric structure (Quanrud et al., 2004). Excepting the HPI fraction, the M_w of the other four fractions decreased significantly during the sequential CEPT and TF operation (especially for the TF unit), indicating that the majority of the hydrophobic and acidic macromolecular fraction could be effectively flocculated, decomposed and biodegraded. In contrast, the low M_w value increase of HPI after CEPT treatment might be ascribed to newly produced HPI via coagulation, and these hydrophilic components could be partially biodegraded during subsequent TF treatment (M_w decreased from 3062 to 1294 Da). It also can be noted that the high M_w values of HPO-A and HPO-N were efficiently removed in the CEPT unit (78.4% for HPO-A and 52.2%

for HPO-N), implying that the high M_w fractions were easy to remove through coagulation. The other two middle M_w value fractions were focused on biodegradation for removal in the TF unit (90.9% for TPI-A and 98.3% for TPI-N). The ratio of d of the different effluents decreased in the trend of: domestic water (211) > CEPT effluent (166) > TF effluent (28), demonstrating that the macromolecular material in raw wastewater could either be precipitated in CEPT units and/or destroyed in the subsequent biological TF units. Notably, the decreased d values for HPO-A, HPO-N, TPI-A and TPI-N fractions during TF operation implied that the organics were efficiently biodegraded. Furthermore, new HPI was biologically produced during the biodegradation process, as indicated by an increased d value for HPI after TF operation.

2.4 Changes in UV-254 and SUVA during CEPT-TF operation

UV-254 and SUVA usually defines the aromaticity of DOM (Leenheer and Croue, 2003; Weishaar et al., 2003). The average UV-254 reduction of the CEPT-TF system was 48.5%, in which the majority of the aromatic components were removed by the CEPT (accounting for 64.7% of the bulk UV-254 reduction), indicating that the coagulation played a major role in the reduction of aromatic components. The UV-254 removal efficiency of the CEPT-TF system was much lower than that for DOC (**Figs. 3 and 4**), ascribed to the preferential removal of non-aromatic fat, long aliphatic carbon and hydrocarbon during aerobic biodegradation in the TF unit.

Fractionation results (**Fig. 4a**) indicated that HPO-A was the predominant aromatic fraction in raw wastewater (contributing 60.1% of the bulk UV-254), followed by TPI-A (12.9%), HPO-N (11.4%), HPI (9.9%), and TPI-N (5.7%). Generally, 38.1% of the aromatic materials in HPO-A could be preferentially coagulated by the CEPT, much higher than that removed in the TF unit (23.8%), indicating that the hydrophobic aromatic fractions could be preferentially removed by coagulation instead of biodegradation. Thus, fly ash could be used as a low-cost coagulant

Fig. 4 Fractional UV-254 (a) and SUVA (b) distribution of DOM in domestic wastewater and CEPT-TF effluents.

material for the removal of aromatic components in raw wastewater. In addition, the UV-254 removal of HPI and TPI-N were quite low during the TF unit operation, implying that part of these hydrophilic aromatic components were newly produced during the aerobic biodegradation.

As shown in **Fig. 4b**, HPO-A tended to exhibit greater aromaticity ($\text{SUVA} = 1.7 \text{ L}/(\text{m}\cdot\text{mg})$) and higher reactivity in forming THMs upon chlorination, while that of HPI was the lowest ($\text{SUVA} = 0.1 \text{ L}/(\text{m}\cdot\text{mg})$). The SUVA value of the other three fractions showed a decreasing trend of HPO-N ($1.0 \text{ L}/(\text{m}\cdot\text{mg})$) > TPI-N ($0.9 \text{ L}/(\text{m}\cdot\text{mg})$) > TPI-A ($0.7 \text{ L}/(\text{m}\cdot\text{mg})$). Those results confirmed the findings that aromatic compounds were abundant in these hydrophobic fractions. Overall, the SUVA value of the hydrophobic DOM fractions of the raw wastewater slightly decreased after the CEPT operation (15.5% for HPO-A and 14.6% for HPO-N), indicating that these hydrophobic macromolecular materials would be partially flocculated by the modified fly ash coagulant. For comparison, the SUVA values of all five fractions in the TF effluent showed a significant increase when the TF unit progressed (especially for the HPI fraction), suggesting that non-aromatic components were preferentially biodegraded by the biomass. These results are quite similar to the findings of Xue et al. (2009).

2.5 FT-IR spectroscopic analysis during CEPT-TF operation

FT-IR spectroscopy has been widely used for gross characterization of DOM, and can provide valuable information on the structural and functional properties of DOM (Chen et al., 2002). According to the previous research (Barber et al., 2001; Kim and Yu, 2005; Kanokkantung et al., 2006a), four DOM fractions (HPO-A, HPO-N, TPI-A and TPI-N) in domestic wastewater were characterized by the aliphatic components ($2950\text{--}2850 \text{ cm}^{-1}$), aromatic C=C peak (1600 cm^{-1}), carboxylic acids ($1720\text{--}1640 \text{ cm}^{-1}$) and carbohydrates ($1250\text{--}1050 \text{ cm}^{-1}$). Aromatic materials were found to be more abundant in the acidic fractions (HPO-A and TPI-A), whereas carbohydrate was predominant in the neutral fractions (HPO-N and TPI-N) instead. The FT-IR spectrum of the DOM fractions (especially for acidic fractions) changed insignificantly during the CEPT process, while new peaks appeared after TF treatments. Thus, aerobic/anaerobic biodegradation seems to be the main reason for the structure changes of DOM during the CEPT-TF operation.

From the spectra of HPO-A (**Fig. 5**), a strong C=O peak at $1730\text{--}1710 \text{ cm}^{-1}$, O–H peak at about $1400\text{--}1370 \text{ cm}^{-1}$, and carbohydrates peak at $1250\text{--}1050 \text{ cm}^{-1}$ clearly demonstrated that carboxylic acids existed as major functional groups in HPO-A. In addition, a shoulder peak at about 1640 cm^{-1} also indicated the abundant existence of aromatic C=C. The intensity of the aromatic C=C peak decreased significantly after the CEPT operation, indicating that the aromatic C=C components could be

preferentially flocculated within the CEPT unit, which was quite consistent with the result of UV-254. By contrast, the aromatic C=C peaks in HPO-A slightly increased when the TF operation progressed, implying that the non-aromatic groups in HPO-A were preferentially removed via biodegradation. In addition, the newly produced peaks at $3100\text{--}3000 \text{ cm}^{-1}$ in the post-TF HPO-A indicated the new production of aromatic structures as a result of biodegradation. The transformation of the hydrocarbons ($1250\text{--}1050 \text{ cm}^{-1}$) in HPO-A was similar to that of the C=C related components, indicating a well-functioning biomass in the TF unit.

The intensity changes of the HPO-N related C=C peaks (1600 cm^{-1}) were similar to those of HPO-A, indicating that the aromatic components in HPO-N could be easily coagulated rather than biodegraded. The intensity increase of $1250\text{--}1050 \text{ cm}^{-1}$ in HPO-N for the CEPT effluent indicated that the hydrocarbon-related components could not be efficiently coagulated, whereas the decreased intensity in the post-TF effluent implied that these materials might be efficiently biodegraded. The removal trend of the carboxylic acid ($1720\text{--}1640 \text{ cm}^{-1}$) components in HPO-N was similar to that of the hydrocarbons.

The intensity distribution of the TPI-A related FT-IR spectrum was similar to that of HPO-A, which can be ascribed to their similar acidic characteristics. Notably, a lower intensity of the TPI-A related C–H peaks ($2950\text{--}2850 \text{ cm}^{-1}$) demonstrated that the content of aliphatic C–H components was relatively lower. The significantly decreased C=C related groups (THMs precursors) in TPI-A after CEPT operation indicated that aromatic groups were effectively removed via coagulation, consistent with the results of SUVA. On the other hand, the slightly decreased intensity of the peaks at 1720 cm^{-1} indicated that carboxylic acids in TPI-A were partly destroyed during the biodegradation within the TF unit. In addition, the slightly increasing intensity of the peaks at 1450 cm^{-1} implied that some new nitrogen-containing compounds were formed in the TF unit.

The slight narrowing of the C=O peaks (at 1720 cm^{-1}) and C=C peak ($1640\text{--}1560 \text{ cm}^{-1}$) in TPI-N after CEPT operation suggested that these carboxylic and aromatic components could be efficiently coagulated. On the contrary, TPI-N became more carboxylic as TF progressed, quite consistent with the results of SUVA. The transformation of the C–H peaks (at 1380 cm^{-1}) showed a converse trend during the CEPT-TF operation.

The major processes governing the transformations of DOM in CEPT-TF system include coagulation and aerobic/anaerobic biodegradation, in which coagulation predominated in the CEPT unit, while aerobic/anaerobic biodegradation prevailed in the TF instead. Thus, the combination of the CEPT and TF units was meaningful for the increased removal of both hydrophobic and hydrophilic components.

Fig. 5 FT-IR spectra for DOM fractions in raw wastewater (line a), effluent of CEPT (line b) and effluent of TF (line c).

2.6 Fluorescence of DOM and fractions during CEPT-TF operation

As shown in **Fig. 6a**, four principal excitation-emission matrix (EEM) peaks were found in the raw domestic wastewater DOM. In general, peaks in the range of Ex/Em 260–400 nm/380–480 nm are associated with humic-like substances, while peaks in the range of Ex/Em 230–260 nm/380–480 nm represent fulvic-like compounds (Senesi et al., 1991). The third fluorophore in the range of Ex/Em 230–260 nm/330–380 nm is related to aromatic protein-like compounds, such as tyrosine, and the fourth fluorophore in the range of Ex/Em 260–360 nm/300–380 nm is related to soluble microbial byproduct-like (SMP-like) materials.

The EEM spectrum of raw wastewater was dominated by SMP-like and protein-like fluorophores, and also showed shoulder humic-like and fulvic-like peaks. As indicated in **Fig. 6b**, the intensity of all four fluorescing compounds decreased substantially during the CEPT operation, especially for fulvic-like fluorophores. In addition, a substantial red-shift was also observed for all four EEM peaks in comparison to that of the raw wastewater. In general, a red shift is associated with the new production of

large molecules through the fly ash coagulant, such as an increase in the number of aromatic rings, or a production of conjugated bonds in a chain structure, such as carbonyl, hydroxyl and amine (Wang et al., 2010). The above results demonstrated that although part of the fluorescent materials in the raw wastewater was significantly coagulated by the fly ash-based coagulant, some macromolecular-related fluorophores were also formed after the coagulation.

The intensity increase of the aromatic protein-like fluorophore for the TF effluent suggested that new aromatic protein-like fluorescing compounds were produced by bacterial metabolism (**Fig. 6c**). Similarly, the fluorescent intensity of the fulvic-like compounds showed a decreasing trend of TF effluent > raw wastewater > CEPT effluent, implying that the fulvic-like compounds could be preferentially removed via coagulation rather than biodegradation. Biodegradation within the TF unit resulted in significant structural changes in humic-like substances. For example, a significant fluorophore in the range of Ex/Em 260–400 nm/380–480 nm was observed for the TF effluent, while this was less significant for the raw wastewater and CEPT effluent. These observations suggested that aerobic biodegradation was the main reason for the structural

Fig. 6 Fluorescence EEMs for DOM and the corresponding fractions in raw wastewater (a), effluent of CEPT (b) and effluent of TF (c).

changes of the fluorescing substances during the CEPT-TF system operation.

The fluorescence intensity of the aromatic protein peak and SMP-like peak were decreased in the EEM spectrum of CEPT effluents. These results suggested that coagulation and flocculation during CEPT operation could lead to their removal or breaking down into non-fluorescent structures (**Fig. 6b**). In contrast, the corresponding intensity of the aromatic protein and SMP-like fluorophores increased significantly after TF operation, implying that the coal cinder was feasible for natural growth of the biomass. Besides, DOM removal in the TF unit could be achieved simultaneously by biodegradation and adsorption on the coal cinder within such systems.

2.7 Economic evaluation

To be able to operate wastewater treatment plants at low energy consumption is welcome in practice, especially for small towns in China. Traditionally, the biological treatment consumes about 65% of the total energy (mainly for aeration) during the operation of a wastewater treatment plant (Pipyn et al., 1994). It was noteworthy that the CEPT-TF system had many advantages such as smaller footprint for construction, no requirement of artificial aeration, and easy operation, which is meaningful for reducing the operating cost of wastewater treatment. For the TF unit, the aeration was achieved via natural ventilation through the multi-layer structure's space, which could save about 65% of the total operational cost in comparison with artificially aerated biological processes.

The observed low sludge production was another feature of the CEPT-TF system. In this study, the CEPT unit produced only a small amount of chemical sludge (0.004 m^3 per cubic meter of wastewater, $\text{SS} = 22 \pm 8 \text{ g/L}$) consisting of suspended solids and colloidal particles present in raw wastewater. The TF unit also produced a very small volume of biofilm sludge (0.28 g/day), which was easily treated and disposed of subsequently, saving operational costs for sludge management.

In addition, the utilization of the fly ash (solid waste) and coal cinder for coagulant preparation and TF packing medium would partially decrease the investment and operational cost of the CEPT-TF process.

3 Conclusions

The CEPT-TF system was shown to be a simple and economical process for treating domestic wastewater in small counties and towns. The following conclusions can be drawn based on the experimental results: (1) HPI, HPO-A and HPO-N were the predominant fractions in raw wastewater. Hydrophobic materials could be preferentially removed by CEPT while the hydrophilic fraction by TF instead. An average of 76.9% of DOC in the influent was removed by CEPT-TF operation, of which TF contributed 70.5% of the bulk DOC reduction. (2) The apparent M_w distribution of DOM fractions showed HPO-A had the highest M_w value and HPI had the lowest value in domestic wastewater. (3) The average UV-254 reduction of the CEPT-TF system was 48.5%, of which 64.7% of the UV-254 reduction was achieved during the operation of the CEPT. HPO-A was the predominant aromatic fraction in raw wastewater (contributing 60.1% of the bulk UV-254), and coagulation played a major role in aromatic HPO-A removal. On the other hand, the non-aromatic materials were preferentially biodegraded in the TF unit. (4) The intensity of the aromatic C=C peak (humic-like fluorophore) decreased significantly in the CEPT unit and increased in the TF unit, implying that CEPT played a major role in the reduction of aromatic components or formed some new aromatic macromolecular materials. The transformations of the hydroxyl C-H and hydrocarbon in natural fractions were the converse of the C=C components.

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