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Fouling control in ultrafiltration of secondary effluent using polyaniline/TiO_2 adsorption and subsequent treatment of desorption eluate using electrochemical oxidation

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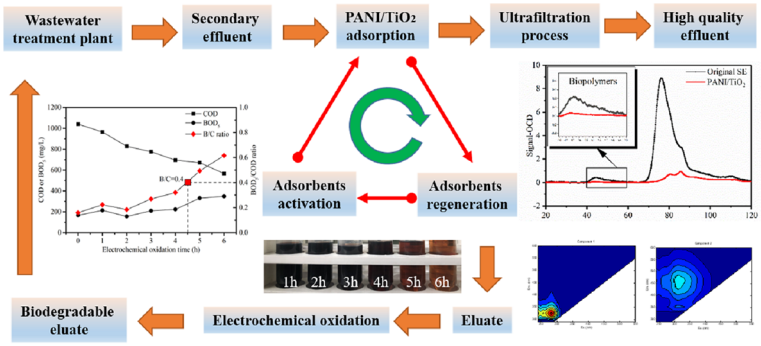
HIGHLIGHTS

- Adsorption-oxidation combined process was used to treat secondary effluent.
- PANI/TiO_2 exhibits excellent performance in the removal of EfOM.
- PANI/TiO_2 alleviated membrane fouling by specifically removing biopolymers.
- Electrochemical oxidation is a potential technology for desorbed eluate.
- BOD_5/COD ratio of eluate can reach > 0.4 after 4.5 h of electrochemical oxidation.

GRAPHICAL ABSTRACT



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ABSTRACT

Performance of three adsorbents, polyaniline-modified TiO_2 (PANI/TiO_2), Dow resin IRA(a) and Dow resin IRA(b), in removing organics from secondary effluent (SE) was evaluated, and the objective of this study is to deliver a treatment loop including membrane fouling control using adsorption and treatment of correspondingly formed desorption eluate using electrochemical oxidation, so that the contaminants could be effectively handled within a wastewater treatment plant. Results show that PANI/TiO_2 is a promising adsorbent in the removal of effluent organic matter (> 55%) and its regeneration was superior to the two others. Specifically, PANI/TiO_2 could remove over 70% of the fraction of biopolymers from the SE and therefore alleviated subsequent membrane fouling to a large extent, while the other two presented less antifouling effect due to limited removal of the major foulants, though they both showed comparable effect as PANI/TiO_2 in the removal of other organic fractions. BOD_5/COD of the concentrated desorption eluate was gradually increasing along with the extension of the electrochemical oxidation. It reached > 0.4 after 4.5 h of treatment, which is of suitable biodegradability for recycling to the influent of the wastewater treatment plant. The improvement on BOD_5/COD was due to the mineralization of effluent organic matter and simultaneous minifying of their molecular size. Moreover, the operation cost of the treatment loop was estimated at about 0.12–0.15 USD/m^3 for delivering effect fouling control and significant improvement on effluent quality.

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1. Introduction

The impact of secondary effluent (SE) discharged from wastewater treatment plants (WWTPs) on the healthy condition of natural water bodies has continuously raised the public's concern [1]. To improve the effluent quality, tertiary treatment using membrane technologies aiming at removing organics [2] has been more and more employed. Nevertheless, membrane fouling is the barrier limiting the widespread of membrane technology [3]. With the improved understanding about foulants in SE [4–6], the removal of one of the key foulants, biopolymers, is getting increased interest [7–9]. Especially in China, the more and more stringent effluent discharge standards have pushed a number of WWTPs improving their treatment efficiency and effluent quality using membranes [10].

In membrane processes, pre-treatment using adsorption has been considered as one of the best practice [11] improving the effect on fouling control [12,13]. In this process the most commonly used adsorbent is activated carbon (ACs, granular or powered) because of its simple operation and high efficiency [14–16]. Nevertheless, both the regeneration possibility and the capacity of fouling control of ACs are limited, therefore some modifications on ACs were studied [17]. Polymeric resins, or ion-exchange resins, were suggested to be alternatives to ACs due to their efficient removal of contaminants [18,19] and high potential in regeneration [20]. Unfortunately, they have lower specific surface area, and thus bring higher investment costs compared to ACs [21]. To overcome the limitations of traditional materials, polymer-based organic-inorganic composites, which present outstanding mechanical properties and compatibility, have received increasing attention in environmental application [22–25]. Wang et al. designed and synthesized a novel adsorbent, polyaniline-modified TiO_2 (PANI/TiO_2), showing excellent adsorption and regeneration abilities. Meanwhile, this adsorbent had outstanding performance in removing dyes from industrial wastewater [26,27], and showed exceptional photocatalysis and antibacterial properties [28]. Considering its specific features (thermo stability, electrical conductivity, etc [29]), it is of great interest to investigate its capacity in treating SE regarding the removal of membrane foulants under corresponding water chemistry conditions.

As the adsorption capacity of adsorbents is limited, the efficiency of desorption and subsequent treatment of desorption eluate need to be addressed as they affect the overall operational cost and bring also negative impact on the environment. However, these issues have not got enough attention in previous studies, especially with respect to the treatment of desorption eluate which is rich in contaminants with high concentration of COD and should be handled within a treatment loop to reduce its impact on the environment. Among advanced treatment methods, electrochemical oxidation has been intensively investigated for its high efficiency in removing recalcitrant pollutants, COD, color [30], total nitrogen (TN) or ammonia [31], and even turbidity [32]. Thus, it could be a candidate in the treatment of the desorption eluate. Considering the amount and the property of the reluctant contaminants in the eluate after the desorption, it would be wise to improve the ratio of biochemical oxygen demand to chemical oxygen demand (BOD_5/COD), so that most of the solution could be returned to the influent of the WWTP, and thus form a relatively safe and environmentally friendly treatment loop.

In this work, the performance of PANI/TiO_2 and two commercial ion-exchange resins (the screened Dow resin) on the removal of effluent organic matter (EfOM) from SE was evaluated. Characterization methods, including size-exclusion chromatography-organic carbon detection-organic nitrogen detection (LC-OCD-OND) [33] and fluorescence excitation emission matrices coupled parallel factor analysis (FEEM-PARAFAC) [34], were employed to understand relevant mechanics of the adsorption in mitigating membrane fouling. Furthermore, the desorption eluate was treated by electrochemical oxidation and it's proved that the biodegradability of the eluate was significantly improved. The core idea of this study is to understand the mechanisms of the promising performance of PANI/TiO_2 in SE treatment and give a solution to handle correspondingly generated desorption eluate. So that these advanced treatment processes could be integrated into the treatment loop within WWTPs. At the end the economic evaluation was conducted to give an insight to the competitive cost efficiency of the whole treatment.

2. Material and methods

2.1. Analysis of water quality

In this study the conventional water quality parameters including humic acid (HA), protein content, polysaccharides content, total organic carbon (TOC), pH and electrical conductivity (EC), were determined using ultraviolet spectrophotometry (UV_{254}), Lowry method, Anthrone-Sulfuric acid colorimetry, TOC auto-analyzer (vario TOC, Elementar Analysensysteme GmbH, Germany), pH probe (STARTER 2100, Shanghai Precision Science Instrument Co., Ltd., China) and conductometer (HQ30d, HACH, US), respectively. For the adsorption test, the SE was collected from a municipal WWTP in Xi'an, China, which had basic water quality information as follows in Table 1:

2.2. LC-OCD-OND and FEEM-PARAFAC

LC-OCD-OND (DOC-LABOR, Dr. Huber, Germany) is a size-exclusion chromatography coupled with organic carbon detector, organic nitrogen detector and UV-absorbance detector, which can be applied to separate the organic matters in water into five fractions based on their molecular weight [33]. In short, this system can measure the molecular weight distribution of organic matters in water. Data acquired were processed by ChromCALC (DOC-LABOR, Karlsruhe, Germany) to quantify the content of biopolymer, humic substances, etc. in the unit of ppb C.

Fluorescence spectroscopy is a sensitive technique used for tracing the dynamics of organic matters and FEEM provides a wealth of information about it. In this study FEEMs of water samples were measured by a three-dimensional fluorescence spectroscopy (FluoroMax-4, HORIBA, US) in excitation wavelength (Ex) from 240 to 500 nm and emission wavelength (Em) from 290 to 550 nm with steps and slits both set to 5 nm. Parallel factor analysis was conducted with Matlab 2014b (MathWorks, Massachusetts, US) by following Stedmon el al.'s tutorial of FEEM-PARAFAC [34]. The components were identified with Chen et al.'s work about interpretation of FEEMs [35].

2.3. Characterization of adsorbents

Composite adsorbent PANI/TiO_2 was synthesized via the in situ chemical polymerization of aniline monomer in the as-prepared TiO_2 solution, with detailed instruction from Wang et al.'s work [27]. Two

Table 1
Basic information of the original SE.

Parameters	Value*
HA	18.2 mg/L
protein	6.4 mg/L
polysaccharides	3.1 mg/L
TOC	7.9 mg/L
pH	7.52
EC	866 μs/cm

*Average value obtained from three times measurement.

Table 2
Detailed information about the tested adsorbents provided by the manufacturers.

	PANI/TiO_2	IRA(a)	IRA(b)
Properties	conductive polymers and inorganic particles	Amberlite strong anion exchangers	
Matrix	polyaniline-TiO_2	styrene-divinylbenzene (gel)	
Functional group	Amino, carboxyl and hydroxyl groups	quaternary ammonium functional group	
Water content	/	49–55%	58–64%
True density	1.03	1.06–1.10	1.05–1.08
Bulk density	/	670 g/L	700 g/L
Particle size range	1–3 um	260–500 um	380–520 um
S_{BET}	6.168 m^2/g	6.078 m^2/g	7.720 m^2/g

ion-exchange resin adsorbents IRA(a) and IRA(b) were purchased from Dow Resin Co., Ltd., China (detailed information was delivered during purchase and can be seen in Table 2). The characterization of the adsorbents included scanning electron microscopy (SEM) with a scanning electron microscope (SNE-3200 MB, SEC Co., Ltd, Korea, S Fig. 1), the Brunauer–Emmett–Teller surface area (S_{BET}) with a fully automatic fast surface area and porosity analyzer (Gemini VII 2390, Micromeritics Instrument Co., Ltd, US, S Fig. 2).

2.4. Pretreatment and chemical cleaning of adsorbents

PANI/TiO_2 was soaked in ultrapure water for 24 h and rinsed 10 times. The clean adsorbent was dried at 50 °C for two hours. 2 g of adsorbent was added to a 50 mL centrifuge tube filled with 40 mL of 0.1 M NaOH solution, and it was shook on a shaker at 200 r/min for 30 min. Then the adsorbent was separated from the NaOH solution by centrifugation at a centrifugal speed of 8000 r/min for 10 min. Thereafter, 40 mL of 0.1 M HCl was added to the centrifuge tube to acidify the PANI/TiO_2, shake and separation processes were the same as in NaOH solution. The acidified PANI/TiO_2 was prepared for adsorption tests. Pretreatments for resins were similar to the procedure treating PANI/TiO_2, the acidified resins were rinsed with ultrapure water until the pH was around 7.

2.5. Adsorption experiments

250 mL of SE mixed with 1 g of pretreated sorbents was stirred on a mechanical stirrer (GTCS-2014, China) at 200 r/min for 300 min. The water quality (with respect to the conventional water quality parameters) was measured at 0, 20, 40, 60, 90, 120, 180, 240 and 300 min during the adsorption test.

Regeneration capacity of adsorbents was evaluated by conducting several adsorption-desorption cycles to see the changes in final removal efficiency of the contaminants. Similarly, 250 mL of SE mixed with 1 g of adsorbents (desorbed and regenerated, detailed processes in section 2.6) was stirred on a mechanical stirrer (GTCS-2014, China) at 200 r/min for 2 h based on preliminary test results. Vacuum filter (SHZ-DIII, Gongyi Yuhua Instrument Co., Ltd., China) was used to separate the adsorbents from the water after adsorption. Water samples were prepared for detailed analysis.

2.6. Desorption and regeneration of adsorbents

The adsorbents (PANI/TiO_2, IRA(a) or (b)) were placed in 50 mL centrifuge tube with 40 mL 0.5 M NaOH solution, stirred on a mechanical stirrer at 200 r/min for 1 h, and then the adsorbents and the eluate were separated by a vacuum filter (SHZ-DIII, Gongyi Yuhua Instrument Co., Ltd., China). After putting the eluted adsorbents into a 50 mL centrifuge tube and acidified using 40 mL of 0.1 M HCl solution, it was further shaken at 200 r/min for 1 h. The mixture was then centrifuged at a speed of 8000 r/min for 10 min. The regenerated adsorbents were continuously used for the next adsorption–desorption cycle.

2.7. Membrane system and fouling characterization

A laboratory ultrafiltration (UF) membrane system (Convergence Inspector, the Netherlands) was set to study the membrane fouling at room temperature about 20 ± 1 °C (schematic diagram could be seen in Supplementary material S Fig. 3). In this setup, PVDF membrane (NADIR® UV150 T, Micodyn-Nadir, Germany) was used for filtration test. The membranes were sealed in a membrane module with filtration area about 80 cm^2. Filtration flux was set as 100 L/m^2 h with a backwash frequency of 15 min. Back wash flux was set at 150 L/m^2 h with backwash duration of 5 min. Transmembrane pressure (TMP) was recorded using a connect computer with a data logging at an interval of each one second. Membrane test was terminated when TMP reached 3.5 bar or filtration and backwash cycle achieved 10 cycles. In this system, the feed was the SE after the treatment of using 4 g/L of adsorbents for 300 min (original SE was used as the control group). The average increasing rate of TMP ($TMP_{ave\text{-}IR}$, bar/cycle), which is defined by Eq. (1) and illustrated in Fig. 3, was used to evaluate the severity of fouling.

$$TMP_{ave-IR} = (TMP_{fN} - TMP_{f1})/N_c \quad (1)$$

where TMP_{fN} refers to the final TMP after each test (bar); TMP_{f1} refers to the TMP at the very beginning of corresponding test; and N_c refers to the times of filter-backwash cycles.

2.8. Eluate treatment using electrochemical oxidation

The eluate was produced by using the same batch of alkali liquor (0.5 M NaOH) for multiple desorption treatment until its COD reached > 1000 mg/L (more detailed procedures are available for reference [26]). The high concentration eluate was treated with electrochemical oxidation in 50 mA/cm^2 current density (anode: PbO_2-PVDF [36] and cathode: Cu). During the electrochemical oxidation process, the solution temperature was controlled at 25 ± 1 °C. Hourly variation of BOD_5 and COD were measured to determine the biodegradability of the treated eluate. Changes in molecular weight distribution and FEEM were also analyzed hourly to understand the variation of the organics in details.

3. Results and discussion

3.1. Comparison of the performance of the adsorbents with respect to TOC removal

Fig. 1 shows the performance of the three adsorbents in removing TOC from the SE. PANI/TiO_2 could remove over half of the TOC from the SE after 40 min of adsorption, and then reached to a removal

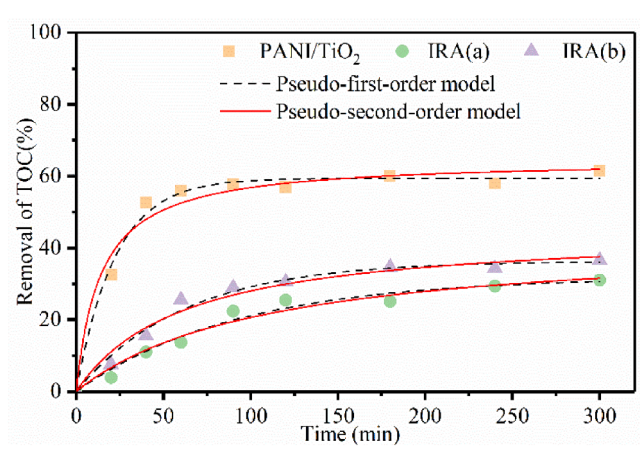

Fig. 1. Kinetics model fitting of TOC removal of three adsorbents.

Table 3
Kinetic parameters of the pseudo-first-order and pseudo-second-order equations for TOC adsorption on three adsorbents.

Adsorbents	pseudo-first-order[a]			pseudo-second-order[b]		
	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	v_0 (mg/g/min)	R^2
PANI/TiO_2	5.34 ± 0.08	0.10 ± 0.01	0.991	5.82 ± 0.21	0.41 ± 0.08	0.975
IRA(a)	2.86 ± 0.17	0.03 ± 0.00	0.976	3.85 ± 0.40	0.04 ± 0.00	0.970
IRA(b)	3.26 ± 0.11	0.04 ± 0.00	0.984	4.06 ± 0.28	0.07 ± 0.01	0.972

[a]Pseudo-first-order model: $q_t = q_e\left(1 - e^{\frac{-k_1 t}{2.303}}\right)$.

[b]Pseudo-second-order model: $t/q_t = 1/(k_2 q_e^2) + t/q_e = 1/v_0 + t/q_e$.

plateau at around 60%. IRA(a) and IRA(b) not only acted slower than PANI/TiO_2, but demonstrated lower adsorption capacity, with a maximum TOC removal less than 40% within 300 min. By fitting pseudo-first-order [37] model and pseudo-second-order [38] model, the adsorption kinetics were investigated (Table 3). According to the correlation coefficient (R^2), the pseudo-first-order model was selected describing the kinetic over the other one. Nevertheless, it was different to some previous results when PANI/TiO_2 was adsorbing dyes, under which condition pseudo-second-order model (chemical adsorption) was identified suitably describing the kinetics [39]. And similar result was observed when Polypyrrole-modified TiO_2 was adsorbing Acid Red G or Methylene Blue [40] and PANI/SiO_2 was adsorbing Phenol [41]. The differences in kinetics may attribute to the highly complicated structure and size distribution of EfOM since the dyes or Phenol was much simpler than EfOM (in Section 3.2, further discussion was made to compare the adsorption of EfOM and model organic substances). Equilibrium adsorption capacity (q_e) showed that per gram of PANI/TiO_2 has theoretically 1.5–2 times higher adsorption capacity than the two others.

In the multiple adsorption-desorption test, Fig. 2 shows that for PANI/TiO_2, the removal of TOC was only slightly decreased (from 63% down to 58%) after ten times of regeneration. In comparison, for IRA(a) and IRA(b), dramatic decrement in TOC removal (25 to 8.4% and 37 to 16%, respectively) could be observed after only five times of regeneration. Based on the above data, it was proved that PANI/TiO_2 was much more recyclable than IRA(a) and IRA(b) considering their regeneration.

3.2. Comparison on the control of membrane fouling

S Fig. 4 shows the increase of TMP using UF treating the original SE. As shown, TMP reached 4.5 bar at the end of the second filtration cycle, and the corresponding $TMP_{ave\text{-}IR}$ was 1.55 bar/cycle, indicating the original SE was of high fouling potential. By contrast, when the feed was treated after using PANI/TiO_2 (Fig. 3(A1)), the TMP reached to less than 0.75 bar even after ten cycles of filtration-backwash, creating a $TMP_{ave\text{-}IR}$ of 0.02 bar/cycle, indicating minor increase of the irreversible fouling. For filtering the SE after IRA(a) and IRA(b) treatment (Fig. 3(A2) and (A3)), it is shown that after seven and nine filtration-backwash cycles, TMP reached over 3.5 bar for both, presenting a $TMP_{ave\text{-}IR}$ of 0.34 and 0.33 bar/cycle, respectively. This is about sixteen folds more than that of filtering the PANI/TiO_2 treated SE. These results indicate that most of the foulants, especially that causes acute irreversible fouling, were much more removed due to the PANI/TiO_2 adsorption compared to that using IRA(a) and IRA(b).

Comparison of the molecular weight distribution of the feed before and after the treatment of different adsorbents is presented in Fig. 3(B1-B3). Paying attention to the retention time during 40–60 min (the enlarged part), which represents the biopolymer (molecular weight > 20 kDa) fraction of the EfOM, the most significant difference among the treatment effect using PANI/TiO_2 and the two others could be identified. The adsorption of PANI/TiO_2 reduced this fraction from 0.28 to 0.08 mg C/L, while that after the treatment of IRA(a) and IRA(b) reached only 0.25 and 0.23 mg C/L, respectively, which means that the residual content of biopolymer after the treatment of PANI/TiO_2 was only about 30% of that after the adsorption using the resins. Looking at the complete chromatograms, Fig. 3 shows that the three adsorbents had high removal on the substances of the retention time during 70–90 min, which represents humic-like substances [33]. Table 4 confirms that PANI/TiO_2 had a slight advantage than the two others in removing humic substances (measured using Anthrone-Sulfuric acid colorimetry method) while they all achieved over 93% removal. As for the fraction of building blocks, the removal of PANI/TiO_2 is 72%, while that of IRA(a) and IRA(b) is 16% and 47%, respectively. The removal on low molecular weight (LMW) neutral was similar to that of building blocks, and these three adsorbents demonstrated similar effect in removing LMW acids. Results of FEEM-PARAFAC (S Fig. 5) agreed with the above findings.

The results of molecular weight distribution analysis and the variation of TMP agreed well with our previous findings that the biopolymers play a key role in UF membrane fouling [2,5]. Because of the removal of this fraction by PANI/TiO_2, the performance of the UF membrane was remarkably improved. At the same time, it can be seen

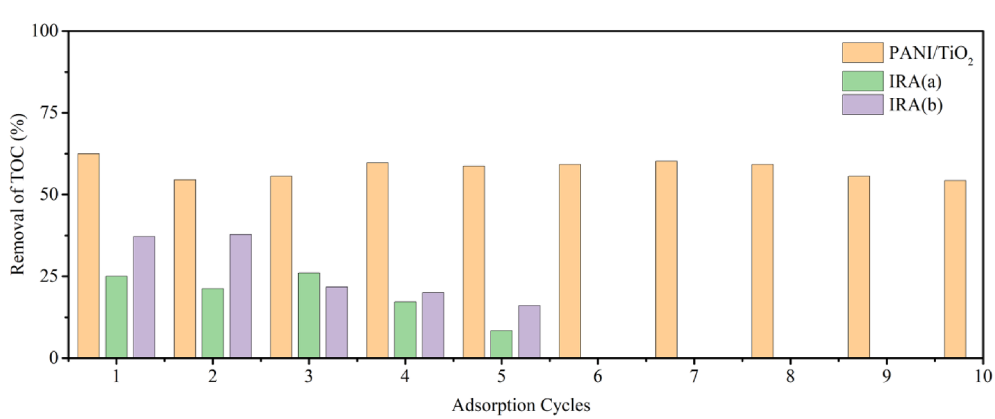

Fig. 2. Multiple adsorption-desorption tests in the removal of TOC.

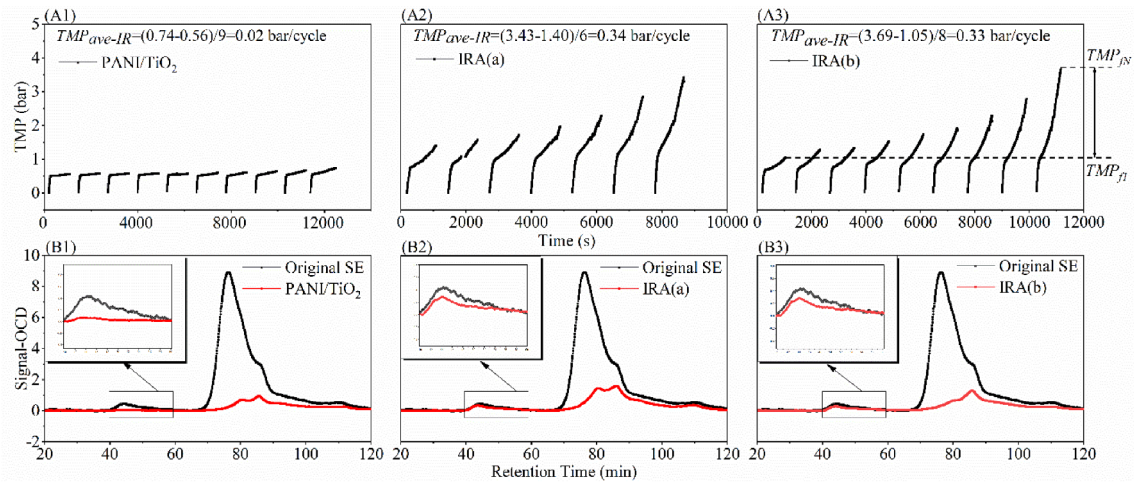

Fig. 3. Variation of TMP during feeding-backwash cycles (A1-A3) and the corresponding molecular weight distribution of the SE before and after treated with adsorbents (B1-B3).

Table 4
Molecular weight distribution (fractions concentration) of original and adsorbents-treated SE (mg C/L).

Samples	DOC*	Biopolymers	Humic substances	Building blocks	LMW acids	LMW neutrals
Feed	7.79	0.28	4.93	0.98	0.06	1.54
PANI/TiO_2 adsorption	1.31	0.08	0.11	0.27	n.q	0.85
IRA(a) adsorption	2.85	0.25	0.33	0.83	n.q	1.44
IRA(b) adsorption	2.08	0.23	0.26	0.52	n.q	1.07

*Dissolved organic carbon, quantified using LC-OCD-OND system.
n.q: not quantifiable, concentration < 1 μg C/L.

that the fractions of humic-like substances and building blocks also play a role with respect to the increase of irreversible fouling. With a similar biopolymer concentration in SE after the treatment of the two resins, higher concentration of humic related substances after the treatment of IRA(a) led to a faster TMP increase than that after IRA(b) adsorption (Fig. 3).

The adsorption and desorption of organics onto/from the adsorbents might be closely related to the functional groups presented on these materials. In which, biopolymers are generally abundant of amino and carboxyl groups and being negatively charged [5], while PANI/TiO_2 is rich in amino, hydroxyl and carboxyl groups [26,27] (also supported by FTIR results in S Fig. 6), the two resins are rich in carbon chains with amino group at their end (information provided by the manufacturers and supported by FTIR results in S Fig. 6). Due to electrostatic attraction and hydrogen bond biopolymers could be readily adsorbed onto PANI/TiO_2. Although humic substances could cover amino groups on the adsorbent and thus reduce binding capacity, the presence of carboxyl and hydroxyl groups on PANI/TiO_2 can still deliver enough binding sites for biopolymers through weak hydrogen binding and Van der Waals affinity [42]. pH went up when NaOH was used to clean PANI/TiO_2. More negatively charged polysaccharides or proteins (important components of biopolymers) led to higher repulsion and resulted in significant desorption effect [43,44], and thus created higher regeneration ability of this adsorbent. In comparison, the dominant presence of amino group on the resins could bind humics superior to biopolymers since the concentration of the humics was 17 times higher than the biopolymers (Table 4), leading to ineffective removal of the big molecules. In chemical cleaning using NaOH, the relatively tight interaction between the different functional groups on resins through electrostatic affinity could not be readily resolved, which might be the main reason of significant loss of their regeneration ability.

To confirm the interpretation of such mechanisms, model substances (proteins, polysaccharides and humic acids) adsorption experiments was conducted (S Fig. 7). It was found that PANI/TiO_2 performed better than the other two adsorbents in the removal of proteins and humic acids, with a final removal of approximately 85% and 83%, while using IRA (a) and IRA (b) the removal of proteins (or humic acids) were only 29% (43%) and 49% (32%), respectively. Multiple adsorption and regeneration results (S Fig. 8) show that after five cycles the corresponding removal of proteins and humic acids using PANI/TiO_2 decreased from 85% and 83% to 76% and 81%, respectively. Though the initial removal of the other two adsorbents was similar to PANI/TiO_2 adsorption, five regeneration cycles resulted in significant reduction in the removal efficiency (averagely only 10% removal for proteins and 30% removal for humic acids was reached then). It is also interesting to see that all these three adsorbents performed poorly in removing polysaccharides from water, with an average removal to around 15%.

Results of the adsorption-desorption experiments using model substances were consistent to the outcomes treating biopolymers using adsorbents by assuming that the predominant components of this fraction are proteins. As shown (S Tab.1), the content of organic nitrogen in biopolymers of the SE was around 64 μg/L with a nitrogen/carbon ratio of 0.24, implying over 70% of the biopolymers are protein-like substances [33], which were preferred to be removed by using PANI/TiO_2 than the other two adsorbents. After the treatment using PANI/TiO_2, the organic nitrogen in the biopolymer fraction decreased to only 4 μg/L (94% removed), while the removal of organic nitrogen was rather low when IRA(a) and IRA(b) was used, with a removal of 24% and 37%, respectively. And, multiple generation cycles didn't affect the performance of PANI/TiO_2 much, implying the adsorbed proteins can be readily desorbed from this material, which is also comparable to the removal performance of model proteins using this adsorbent.

3.3. Eluate treatment using electrochemical oxidation

Electrochemical oxidation results are shown in Fig. 4. BOD_5/COD increased gradually and reached 0.4 after four and half hours of the oxidation treatment. The improved BOD_5/COD implies that the concentrated eluate is much more biodegradable than the original one [45]. After six hours of oxidation, the BOD_5/COD ratio reached even 0.6, indicating the organics became further biodegradable. The increasing trend of BOD_5/COD during the treatment supports that this method is suitable for handling the eluate desorbed from PANI/TiO_2. Turn to the specific energy consumption (calculated, shown in S Fig. 9), it was found that during the oxidation process, the increase of specific energy consumption was increased from 98.5 to 107.4 W·h/(g COD) along with the duration of the treatment from four to six hours (detailed economic analysis was discussed later).

The variation of the LC-OCD-OND chromatogram of the eluate during the electrochemical oxidation treatment is presented in Fig. 5. As shown, the relative content of biopolymers is relatively low in the concentrated eluate compared to that in the SE (Fig. 3 and Table 4). One possible explanation is that the high molecular weight organic matters, including proteins, polysaccharides, etc., might be hydrolyzed to lower molecule weight substances in NaOH solution during chemical cleaning of the adsorbents [46]. Or they might be aggregated during desorption and removed by the pre-filter due to the interaction between high content of proteins and polysaccharides [47,48]. Back to the causes of the improved biodegradability, Fig. 5 shows clearly that along with the oxidation more peaks appeared at longer elution time, indicating the formation of the organics with smaller sizes [33]. The LMW

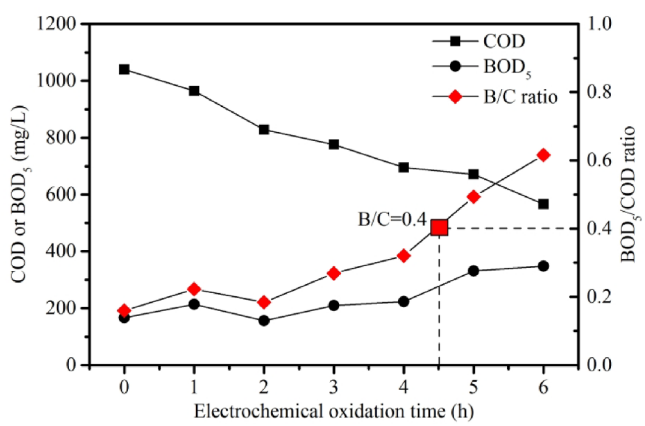

Fig. 4. Variation of COD, BOD_5 and BOD_5/COD ratio during electrochemical oxidation (B/C = BOD_5/COD).

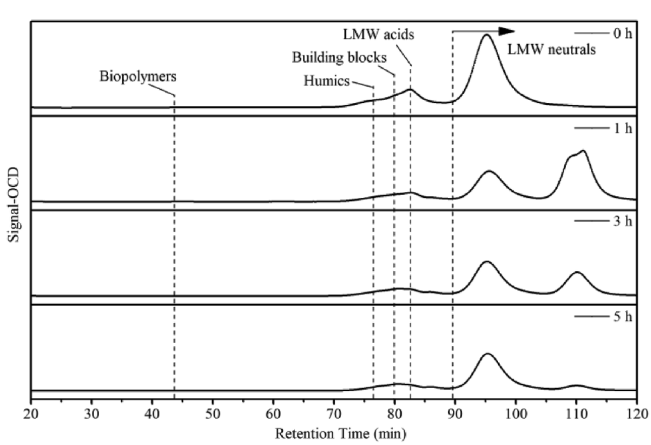

Fig. 5. Variation of molecular weight distribution of original and electrochemical oxidation treated eluate.

Table 5
Molecular weight distribution (fractions concentration) of electrochemical oxidation treated eluate (mg C/L).

Treatment time	DOC	Biopolymers	Humic substances	Building blocks	LMW acids	LMW neutrals
0 h	371.5	4.3	55.2	97.5	n.q	214.5
1 h	328.9	3.5	42.9	77.6	n.q	204.9
2 h	268.9	3.1	39.2	68.2	0.6	157.8
3 h	238.9	2.3	32.5	55.3	2.2	146.6
4 h	196.9	1.7	27.3	50.5	3.5	113.9
5 h	171.2	0.8	25.2	48.1	4.9	92.2
6 h	165.1	0.6	22.1	42.5	5.3	94.6

n.q: not quantifiable, concentration < 1 μg C/L.

acids increased from 0.6 to 5.3 mg C/L during the oxidation (Table 5), indicating that with the electrochemical oxidation treatment, high molecular weight substances were continuously transformed to LMW material, which should be more biodegradable (increased BOD_5/COD in Fig. 4).

A decreasing of the overall dissolved organic carbon (DOC) during the electrochemical oxidation was also recorded (Table 5), which can be attributed to the mineralization of organic matter using electrochemical oxidation [49]. As shown, in the first four hours around 50% of the DOC was removed. The amount of humic substances, building blocks and LMW neutrals were all decreasing during the oxidation. After that, the treatment efficiency was obviously going down, which is consistent with some previous findings that along with the treatment using oxidation, the specific energy consumption would increase [50–52]. Considering both the treatment efficiency and energy consumption, 4.5 h might be an economically suitable treatment duration in the present work.

S Fig. 10 shows the variation of the FEEMs of water samples during the electrochemical oxidation treatment, where gradual fading of the fluorescence signal could be observed. This agrees with the LC-OCD-OND results (Fig. 5 and Table 5). Using PARAFAC analysis, two major components were identified in the desorption eluate (Fig. 6, left). Component 1 had its FEEM peak at $\lambda_{Ex/Em}$ = 280/325, which represents the protein-like substances containing tryptophan (belongs to region IV: soluble microbial byproduct-like substance); while component 2 has its FEEM peak at $\lambda_{Ex/Em}$ = 320/450, which represents model humic acid polymers (belongs to region V: humic acid-like substance). Changes in the intensity of fluorescence (Fig. 6, right) show that component 1 demonstrated a trend of weakening although with some fluctuation while component 2 kept decreasing. This agrees with the quantified results from Table 5, where humic substances contents (correspond to component 2) kept dropping.

3.4. Economic evaluation

The operation cost of the advanced treatment of SE in the present test includes mainly two parts, the PANI/TiO_2 related (purchase and depreciation, pre-treatment and regeneration of the adsorbent) and the electrochemical oxidation treatment related (mainly energy consumption). Information about the price of PANI/TiO_2, chemical reagents, electricity, etc. can be found in Alibaba.com (detailed information in Table 6).

To calculate the operation cost regarding to the TOC removal, necessary assumptions are made below: (1) the treatment capacity of the WWTP is 100,000 m^3/d; (2) objective TOC deduction from SE is 5 mg/L; (3) the maximum regeneration times for PANI/TiO_2 without obvious treatment efficiency decrease is 100 times (announced by the manufacturer); (4) COD of the desorption eluate is 1000 mg/L and the objective is to decrease it to under 650 mg/L (based on our finding that BOD_5/COD could reach above 0.4); (5) specific energy consumption for the electrochemical oxidation treatment is 100 W·h/(g COD) (based on

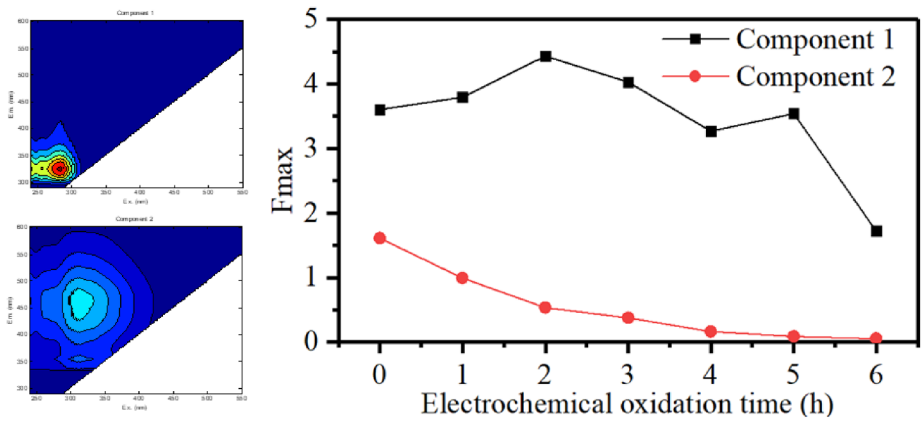

Fig. 6. Variation of fluorescence intensity of components divided by PARAFAC.

Table 6
Estimated operation costs of SE treatment with PANI/TiO_2.

Items	Price	Usage	Costs (RMB)	Contribution (%)
PANI/TiO_2	50,000 RMB/t	0.86–0.94 g/L SE	42955.3–46816.5	46.3
HCl (31%, Liquor)	600 RMB/t	4.70 mL/g PANI/TiO_2	24226.8–26404.5	26.1
NaOH (99%, Solid)	2200–3500 RMB/t	0.4 g/g PANI/TiO_2	7480.0–12950.0	10.5
Electricity	0.7–1.2 RMB/kW·h	100 W·h/g COD	12250.0–21000.0	17.1
		Total costs:	107170.9–86912.1	RMB

the average energy consumption of the six hours electrochemical oxidation treatment in the lab); (6) HCl or NaOH solution for pretreatments, desorption and regeneration of PANI/TiO_2 are reusable for 10 times (based on our regeneration experimental results).

Sections 3.1, 3.2 and 3.3 showed that it takes about one hour to reach the maximum TOC removal and the kinetic models show that theoretically PANI/TiO_2 had a TOC removal capacity of 5.34 ± 0.08 to 5.82 ± 0.21 mg/g in SE. Based on the above experimental findings and calculations (detailed calculation in S Tab. 2), the results are as follows:

According to the calculation, the cost for the treatment of SE using PANI/TiO_2 and electrochemical oxidation is 0.87–1.07 RMB/m^3, equivalent to about 0.12–0.15 USD/m^3. By this treatment the TOC of SE could reach a deduction of 5 mg/L and the BOD_5/COD of the eluate could reach above 0.4, which would make the effluents have a minimal impact on the environment. It could be noticed that the consumption of adsorbents and HCl account for 46.3% and 26.1% of the total operation cost, respectively, which demonstrated that the operation cost mainly depends on the price of the adsorbent and acid. A reduction of the price of PANI/TiO_2 would create great opportunity for the application of such materials in treating SE considering the current policy in China, which requires strict removal of different kinds of pollutants.

4. Conclusions

In this study, the performance of PANI/TiO_2, IRA(a) and IRA(b) in the treatment of SE was compared, and their impact on membrane fouling control was discussed. Moreover, a suitable treatment method for desorption eluate was proposed to create a complete treatment loop. The main conclusions are drawn as follows:

(1) PANI/TiO_2 is a promising adsorbent in the treatment of SE, which could remove around 58% of TOC even after ten times of regeneration. Though IRA(a) and IRA(b) had effects in TOC removal at the first time, their performance degraded quickly along with the increase of the number of regeneration.
(2) In membrane fouling control, PANI/TiO_2 performed the best, followed by IRA(b) and IRA(a). PANI/TiO_2 could adsorb most of the biopolymers from the SE while the other two demonstrated only minor removal of this fraction.
(3) BOD_5/COD ratio of the concentrated eluate increased with the electrochemical oxidation treatment. Considering the treatment efficiency and energy consumption, 4.5 h of electrochemical oxidation was optimal. The mechanisms of better biodegradability after electrochemical oxidation include transformation of high molecular weight organics to smaller ones and simultaneous mineralization.
(4) Economical evaluation results show that the operation costs for SE using PANI/TiO_2 and electrochemical oxidation is 0.87–1.07 RMB/m^3, equivalent to about 0.12–0.15 USD/m^3, with which the TOC of SE could decrease 5 mg/L and the BOD_5/COD of the eluate could reach above 0.4. The main costs for operation was the purchase of PANI/TiO_2 because of its high price currently, followed by HCl utilization (acid chemical cleaning).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2019.122915.

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