

A hybrid process of powdered activated carbon countercurrent two-stage adsorption and microfiltration for petrochemical RO concentrate treatment

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HIGHLIGHTS

- A countercurrent two-stage adsorption–microfiltration (CTA-MF) process was proposed.
- Dissolved organics in petrochemical RO concentrate were removed efficiently.
- A high overall recovery (91%) of reverse osmosis (RO) can be achieved.
- A simple CTA-MF calculation method was established to predict the effluent.

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ABSTRACT

In petrochemical wastewater reclamation, the dissolved biorefractory organics from reverse osmosis concentrate (ROC) is a key obstacle to increasing the overall recovery of reverse osmosis (RO) technology. A hybrid process of countercurrent two-stage adsorption and microfiltration (CTA-MF) was proposed to remove the organics in ROC by powdered activated carbon (PAC). In order to analyze the CTA-MF process, a simple calculation method was established based on the adsorption accumulation principle and response surface methodology (RSM) equations. Approximately 37% of fresh PAC was saved through the CTA-MF process compared with a conventional adsorption process. When the fresh PAC dosage was 0.48 g/L, the average values of chemical oxygen demand (COD) and dissolved organic carbon (DOC) were decreased from 94.1 mg/L and 25.6 mg/L to 36.9 mg/L and 6.98 mg/L, respectively, which coincided well with the predicted results and met the influent requirement of RO for high overall recovery.

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1. Introduction

Reverse osmosis (RO) technology is widely used in seawater desalination and the wastewater reclamation [1], but the application of inland RO technology is limited by the high operation costs and reverse osmosis concentrate (ROC) disposal. The RO recovery is approximately 70% for wastewater reclamation, while the residual ROC is the key obstacle to increasing the recovery further or reducing the discharge of pollutants. The ROC from wastewater treatment plants usually presents higher organic pollutant load (dissolved organic carbon, DOC 19.2–57.2 mg/L; chemical oxygen demand, COD 60–184 mg/L) but lower salinity (total dissolved

solid, TDS 1.1–5.6 g/L) than that from desalination plants in the investigation reported by Pérez-González [2]. In order to achieve the high overall recovery (>90%), antiscalant and chemically-enhanced seeded precipitation technologies [3,4] are used to eliminate the mineral scaling for secondary RO in desalination plants. However, in the ROC from the wastewater treatment plants, especially in the ROC from the petrochemical plants, the dissolved biorefractory organics is the potential fouling matter [5] after sufficient pretreatment through biodegradation followed by microfiltration (MF) or ultrafiltration (UF). The cost-effective approaches are being researched to reduce the organic fouling on RO membrane.

Adsorption on activated carbon is widely employed for the removal of organic matter, and the working adsorption amount of adsorbent could be increased significantly via a countercurrent adsorption process pointed by Tseng [6]. In our previous studies [7], the dissolved organics in ROC from a petrochemical plant could be removed by powdered activated carbon (PAC) adsorption and microfiltration efficiently. However, those results only came from

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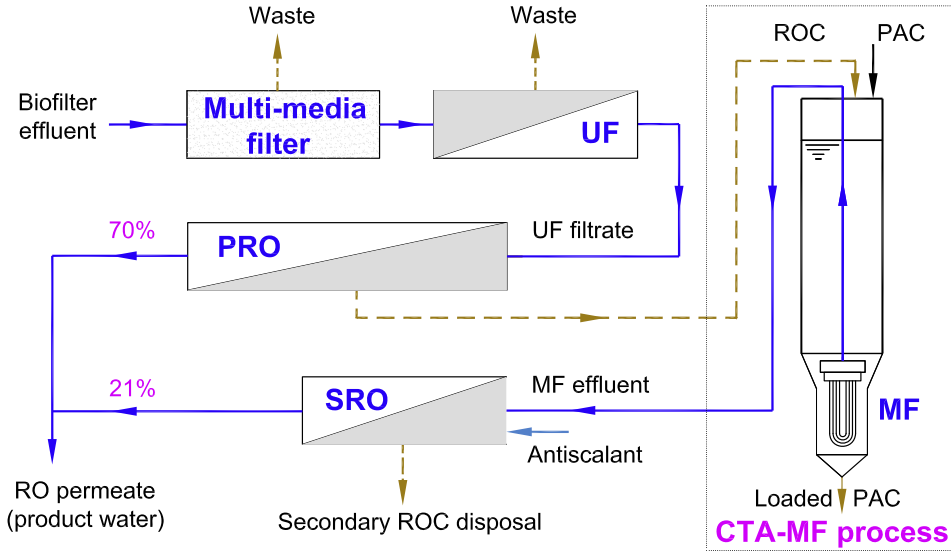


Fig. 1. The application of CTA-MF process for ROC treatment to increase overall recovery.

jar tests, and that hybrid process was not perfect, lacking an integrated calculation method of PAC dosage.

In this paper, a countercurrent two-stage adsorption and micro-filtration (CTA-MF) process was proposed for the high recovery of petrochemical wastewater reclamation (Fig. 1). UF filtrate was first separated in a primary RO (PRO) stage at a recovery of 70%, followed by CTA-MF process to reduce the organic fouling matter from primary ROC. Then, the treated ROC was filtered further in a secondary RO (SRO) stage to achieve the high overall recovery (91%). In addition, the DOC in petrochemical ROC was the removal target and a simple calculation method was established to research CTA-MF process further. The CTA-MF calculation method was satisfactorily verified by lab-scale experiments, and could provide a convenient operation in practical application.

2. CTA-MF process and corresponding calculation method

The schematic diagram of CTA-MF process for DOC removal by means of PAC is shown in Fig. 2. At the initial stage, the primary ROC with a DOC concentration of C_0 and a volume of V was injected into the reactor, contacting with the fresh PAC at a dose of x_1 for a defined adsorption time of t to obtain a mixture with a DOC concentration of C_{e1} . The effective volume of reactor was expressed as V (L). If the adsorption process complies with the Freundlich isotherm, Eq. (1) can then be established [8].

$$\frac{C_0 - C_{e1}}{x_1} = K_{F0} C_{e1}^{1/n_0} \quad (1)$$

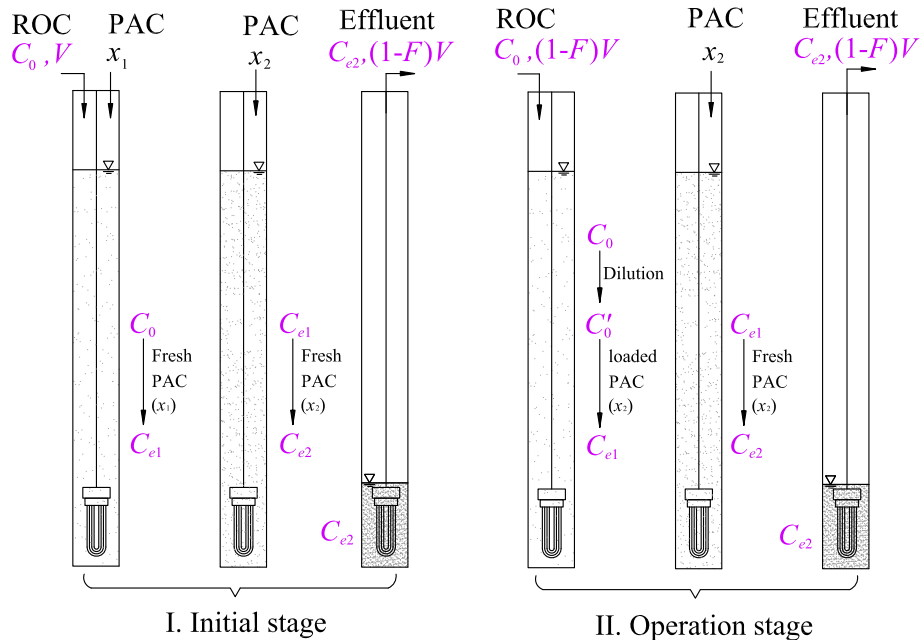


Fig. 2. Schematic diagram of CTA-MF process. Note: 1. the concentration of adsorbate on the loaded PAC can be accumulated, excluding desorption; and 2. the adsorption of the PAC loaded more than twice was excluded.

where C_0 and C_{e1} are the adsorbate concentrations of initial ROC and equilibrium mixture (mg/L), respectively; x_1 (g/L) is the dosage of PAC at the initial concentration of C_0 ; K_{F0} and $1/n_0$ are the Freundlich constants at the initial concentration of C_0 .

Another fresh dose of PAC with a value of x_2 was then added, with the DOC concentration reduced to C_{e2} that could be set based on the treatment requirement after a defined adsorption time. At this point, effluent with a volume of $(1 - F)V$ was withdrawn through the MF membrane and a portion of the mixture with a volume of FV was retained to submerge the MF membrane. The dilution factor F was defined as the ratio of the retention and total solution volumes in the reactor.

At the operation stage in Fig. 2, the injected ROC with a DOC concentration of C_0 and a volume of $(1 - F)V$ was mixed with the remaining solution containing a DOC concentration of C_{e2} with a volume of FV , producing a mixture with a DOC concentration of C'_0 written as Eq. (2) based on the mass balance.

$$C'_0 = (1 - F)C_0 + FC_{e2} \quad (2)$$

where C'_0 and C_{e2} are the adsorbate concentrations of the dilution mixture and equilibrium effluent (mg/L), respectively; the dilution factor F is a coefficient from 0 to 1.

At this point, the DOC of the mixture was adsorbed by the previously loaded PAC with a dose of x_2 . After a defined time, the DOC concentration of the mixture was reduced to C_{e1} . Moreover, the amount of desorption was deemed negligible, and Eq. (3) was established according to the accumulation principle of adsorbate on the loaded PAC and Freundlich isotherm through experimental verification [7].

$$\frac{C_{e1} - C_{e2}}{x_2} + \frac{C'_0 - C_{e1}}{x_2} = K'_{F0} C_{e1}^{1/n'_0} \quad (3)$$

where x_2 (g/L) is the dosage of PAC at the initial concentration of C_{e1} ; K'_{F0} ($\text{mg}^{(1-1/n'_0)}\text{L}^{1/n'_0}/\text{g}$) and $1/n'_0$ are the Freundlich constants at the initial concentration of C'_0 .

After that, a fresh dose of PAC with a value of x_2 was input for a defined adsorption time to obtain an MF effluent with a DOC concentration of C_{e2} ; effluent with a volume of $(1 - F)V$ was then withdrawn. The operation process was then duplicated. A complete operation process was deemed as one MF effluent cycle, including ROC injection, PAC dosage and effluent withdrawal. In order to simplify the equations, Eq. (4) was obtained by substituting Eq. (2) into Eq. (3) and rewriting.

$$\frac{(1 - F)(C_0 - C_{e2})}{x_2} = K'_{F0} C_{e1}^{1/n'_0} \quad (4)$$

The PAC dosage of CTA-MF process can be obtained by calculating the general solutions of Eqs. (1) and (4). In the two equations, C_0 and C_{e2} are the known DOC concentrations of inflow and MF effluent, respectively; K_{F0} , $1/n_0$ and K'_{F0} , $1/n'_0$ are the isothermal parameters from jar tests when initial DOC concentrations are C_0 and C'_0 , respectively; the value of F can be set in advance. However, another equation is needed for the three unknown parameters of C_{e1} , x_1 and x_2 .

A relationship expression can be obtained between the adsorption isotherms and the different initial DOC concentration values due to the change of PAC dosage based on the phenomena of intraparticle diffusion [9], pore blockage [10], and competitive adsorption of different adsorbates [11,12]. In addition, response surface methodology (RSM) experiment is based on statistical mathematics and *Design-Expert* software to design the experiments and analyze the data; the functional relationship between the variables and the response values can be easily obtained [13]. A central composite design method is widely used because the data in the center of the design range are more accurate [14,15]. According to the RSM experimental design, a series of C_{e2} values can be obtained through changing the values of x_1 and x_2 in the experiments, and Eq. (5) was given by the *Design-Expert* software.

Through a trial-and-error procedure, which is called the CTA-MF calculation method, the values of C_{e1} , x_1 and x_2 can be obtained by calculating the general solutions of Eqs. (1), (4) and (5), as shown in the following.

$$\frac{C_0 - C_{e1}}{x_1} = K_{F0} C_{e1}^{1/n_0} \quad (1)$$

$$\frac{(1 - F)(C_0 - C_{e2})}{x_2} = K'_{F0} C_{e1}^{1/n'_0} \quad (4)$$

$$C_{e2} = f(x_1, x_2). \quad (5)$$

3. Materials and methods

3.1. The materials and ROC characteristics

The ROC came from a petrochemical plant and was derived from biologically treated reused wastewater that underwent an ultrafiltration and RO process. The fluctuations of COD and DOC in the ROC were observed over a research period of several months, as shown in Table 1. The other parameters were the average values contained in the ROC. Commercially available analytical grade chemicals were used to determine COD by means of the potassium dichromate oxidation method [16]. The DOC level was determined by using a TOC analyzer (TOC-V_{CPH}, Shimadzu, Japan), and conductivity was determined with a conductivity meter (DDS-307A, Shanghai Leici Instruments, China). The pH values were measured with a precision pH meter (PP-25, Sartorius, Germany). The concentrations of calcium and magnesium ions were measured with an atomic absorption spectrometer (180-80, Hitachi Ltd., Japan), and the chloride and sulfate levels were measured with an ion chromatogram (DX-600, Dionex, USA). These results are listed in Table 1.

Industrial grade coal-based PAC (200 mesh) was purchased from Luda Co., Ltd. in Zunhua, China. Prior to use, the PAC was baked in an electric oven for 1 h at 105 °C to remove moisture. The BET surface area was 867.3 m²/g and the pore size range was 0.36–4.5 nm, which were obtained from 77KN₂ isotherms using a sorptometer (NOVA2200e, Quantachrome Instruments, USA). The minimum iodine value was 680 mg/g, the methylene blue value was 147 mg/g and the maximum ash content was 11.2% which are referred to *Granular Activated Carbon Test* [17].

3.2. Jar tests of kinetics, isotherm and RSM function

For determination of the kinetic parameters, the ROC (0.100 L) contacted with a constant amount of fresh PAC (0.9 g/L) over a range of time (2 to 40 min) in a series of shaking 250-mL conical flasks (200 rpm). The ROC (0.100 L) and pre-weighed fresh PAC (0.1 to 0.9 g/L) were separately added into 250-mL conical flasks that were placed on a shaker for 20 min in isothermal experiments. The experimental temperature was 25 ± 1 °C, and the samples containing PAC

Table 1
Characteristics of ROC.

Parameters	Unit	Value
COD	mg/L	94.14–109.0
DOC	mg/L	25.61–30.33
Conductivity	ms/cm	3.70
pH value	/	7.80
Mg ²⁺	mg/L	70.60
Ca ²⁺	mg/L	134.2
Cl [−]	mg/L	783.1
SO ₄ ^{2−}	mg/L	501.4
TDS	mg/L	2149

were filtered through MF membranes ($0.22\ \mu\text{m}$; mixed cellulose ester; China). The average values of two parallel experiments were reported.

A central composite design method was applied to obtain the RSM function by using *Design-Expert* software. The ROC ($0.100\ \text{L}$) and fresh PAC ($0.02\text{--}0.58\ \text{g/L}$) were mixed for 20 min in a series of shaking conical flasks and then separated by the MF membrane to obtain different effluents. The isotherm experiment with a defined initial concentration was then initiated with fresh PAC ($0.06\text{--}1.04\ \text{g/L}$) in the shaker for 20 min of adsorption time. The significance of the RSM function was determined through variance analysis.

3.3. Lab-scale experiments of CTA-MF process

The experimental schematic of the CTA-MF is shown in Fig. 3. The process operation was controlled by a programmable logic controller (PLC) system.

The temperature was $25 \pm 1\ ^\circ\text{C}$, and pumps were interconnected with a liquid level detector via the PLC. Air was continuously supplied to the MF reactor, and the volume ratio of gas to treated water was 8:1. Maintaining a membrane flux of $27.6\ \text{L/h} \cdot \text{m}^2$, the MF effluent peristalsis pump worked for 10 min and shut off for 1 min, worked for 8 min and shut off for 1 min, and then worked until the mixture reached a low liquid level as controlled by the PLC. The circulation pump worked at $100\ \text{mL/min}$, but shut off in the last 5 min of MF effluent to alleviate the concentration polarization resulting from PAC accumulation. The hydraulic residence time and the treatment capacity of the reactor were $1.04\ \text{h}$ and $2.89\ \text{L/h}$, respectively. The polyvinylidene fluoride MF membrane module ($0.22\ \mu\text{m}$; $0.25\ \text{m}^2$) was provided by Tianjin Motimo Membrane Technology Co., Ltd., China. Depending on the sampling frequency, the appropriate amount of MF effluent was collected in a $25\ \text{L}$ plastic bucket and was well mixed prior to sampling. The replicated samples were recorded, and the average values were reported.

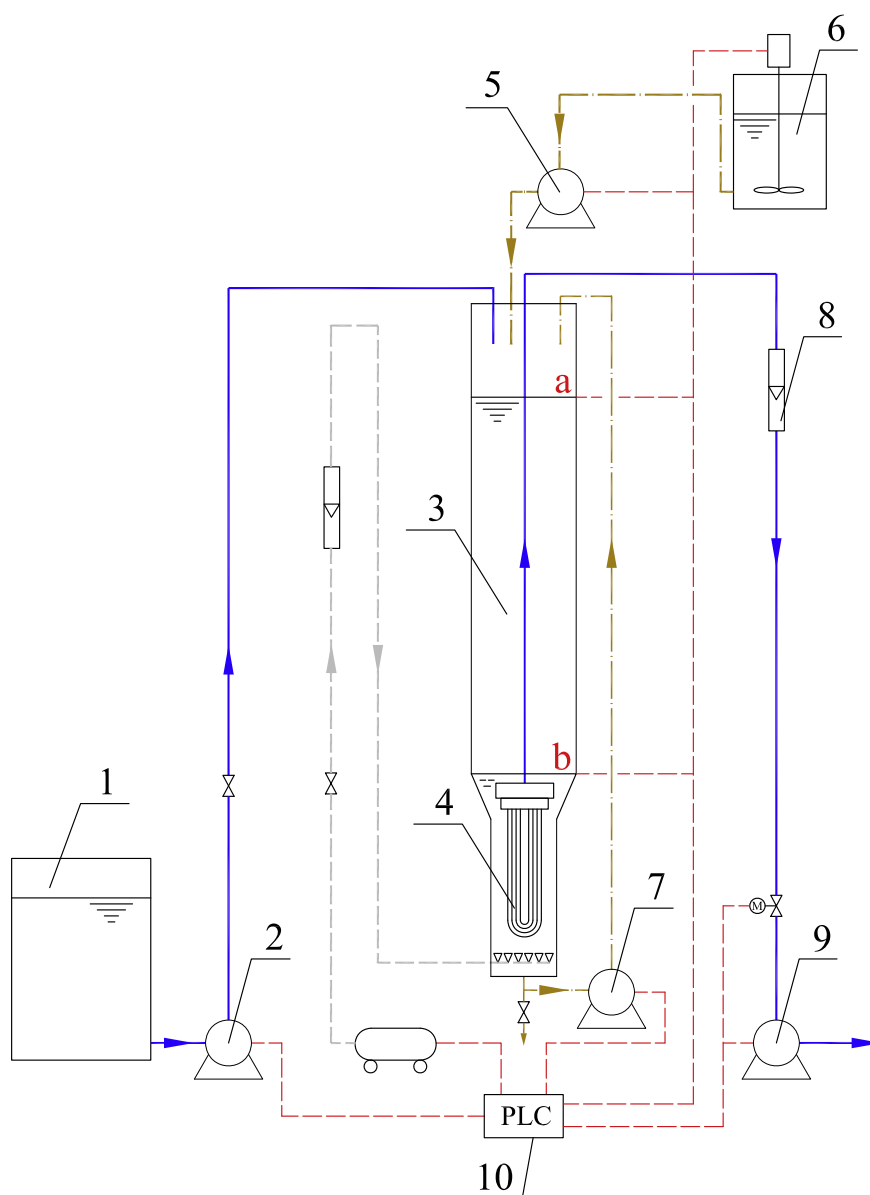


Fig. 3. Schematic device of CTA-MF process. 1 – ROC tank, 2 – feed pump, 3 – reactor, 4 – MF module, 5 – dosing pump, 6 – fresh PAC suspension tank, 7 – circulation pump, 8 – flowmeter, 9 – effluent pump, 10 – PLC, and a, b – liquid level detector.

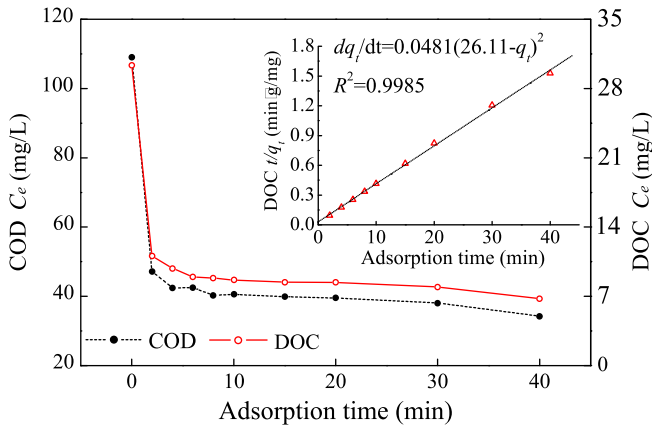


Fig. 4. The effect of adsorption time on COD and DOC removal in ROC (PAC dose of 0.9 g/L).

4. Results and discussion

4.1. Determination of adsorption time

The influence of adsorption time on the MF effluent quality is shown in Fig. 4, and the methods were previously referred to Section 3.2. The decreased trend of DOC and COD values diminish after adsorption for 10 min. Depending on the adsorption efficiency and the hydraulic residence time of reactor, an adsorption time of 10 min should be sufficient. However, considering the MF effluent draw-off pattern, the adsorption time of 20 min was suitable because of the membrane properties and the PAC concentration polarization.

At the operation stage of the CTA-MF lab-scale experiments shown in Fig. 2, most of the adsorption processes had been completed when the fresh PAC with a dose of x_2 was placed into the reactor for an adsorption time of 10 min. The adsorption reaction then continued for approximately 20 min in an MF effluent progression. As a result, the adsorption time for the MF effluent that had been drawn out of the reactor was initially 10 min but eventually 30 min. The average adsorption time was regarded as 20 min if all the MF effluents were completely mixed. Therefore, an adsorption time of 20 min was selected for the determination of the isothermal parameters in jar tests, RSM experiments, and CTA-MF lab-scale experiments. A pseudo-second-order kinetic rate equation [18] can be described as Eq. (6). Kinetic parameters were calculated according to Eq. (6) and are shown in Fig. 4.

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e^2 k_2} \quad (6)$$

Table 2
The design and results of RSM experiments.

No.	PAC x_1 (g/L)	PAC x_2 (g/L)	$C_{e2(COD)}$ (mg/L)	$C_{e2(DOC)}$ (mg/L)
1	0.5	0.9	38.58	6.439
2	0.3	1.04	34.65	6.470
3	0.58	0.55	37.80	6.283
4	0.1	0.9	44.88	8.914
5	0.3	0.55	43.47	7.742
6	0.3	0.55	44.09	8.014
7	0.3	0.55	42.52	8.161
8	0.3	0.55	40.95	8.027
9	0.3	0.55	38.98	8.282
10	0.5	0.2	45.12	10.24
11	0.02	0.55	51.02	13.77
12	0.3	0.06	54.17	14.63
13	0.1	0.2	65.59	17.87

ROC: COD = 109.0 mg/L, DOC = 30.33 mg/L.

where q_t and q_e are the adsorption capacity of PAC at time t and at saturation (mg/g), respectively; and k_2 is the pseudo second-order kinetics constant (g/(mg · min)).

4.2. Determination of RSM functions

The design methods and ranges were carefully selected to ensure the accuracy of the RSM function. The design ranges of x_1 and x_2 were 0.1–0.5 g/L and 0.2–0.9 g/L, respectively. The RSM experiments were referred to Section 3.2; the design and results were shown in Table 2.

The results of Table 2 were entered into the software, and the functions of C_{e2} described by DOC and COD were written as Eqs. (7) and (8), respectively.

$$C_{e2(DOC)} = 25.739 - 40.085x_1 - 26.743x_2 + 18.411x_1x_2 + 28.376x_1^2 + 11.402x_2^2 \quad (7)$$

$$C_{e2(COD)} = 80.210 - 89.807x_1 - 54.862x_2 + 50.607x_1x_2 + 55.928x_1^2 + 18.262x_2^2 \quad (8)$$

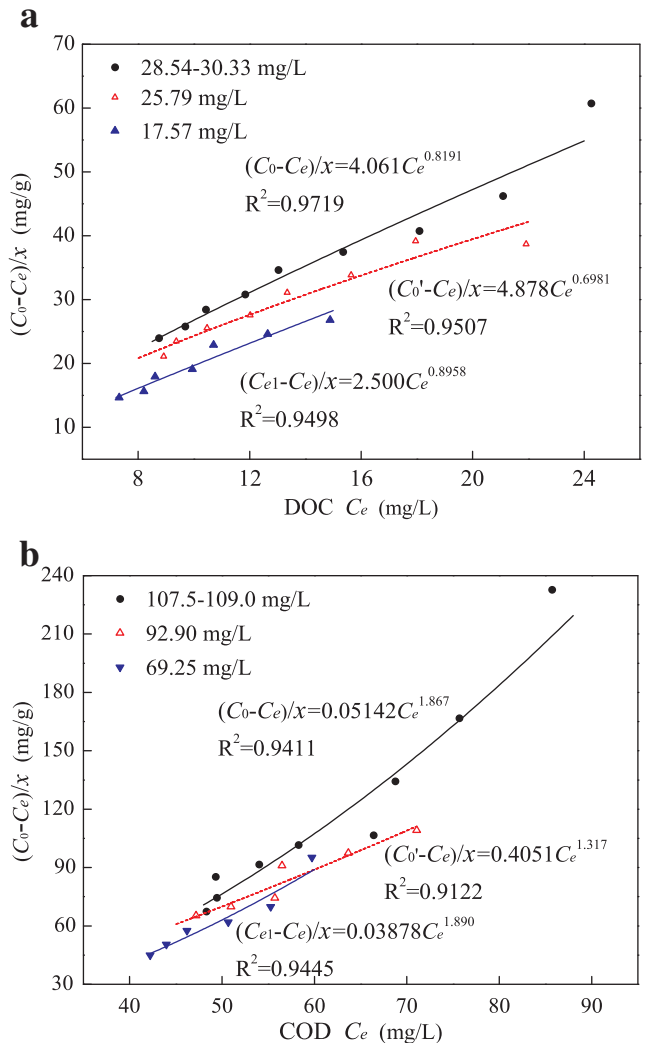


Fig. 5. The effect of different adsorbate initial concentrations on adsorption isotherms in experiments. (a) DOC: $C_0 = 30.33$ mg/L, $C_0' = 25.79$ mg/L, $C_{e1} = 17.57$ mg/L; and (b) COD: $C_0 = 109.0$ mg/L, $C_0' = 92.90$ mg/L, $C_{e1} = 69.25$ mg/L.

4.3. Calculation of PAC dosage

The calculation process of PAC dosage begins with DOC removal. The isothermal parameters of K_{FO} , $1/n_0$ and $K_{FO'}$, $1/n_0'$ should be obtained from experiments before solving the CTA-MF calculation method. The values of K_{FO} and $1/n_0$ obtained from a particular initial concentration C_0 (30.33 mg/L) and shown in Fig. 5a were assumed to be the applicable parameters within the range of DOC fluctuation shown in Table 1 (25.61–30.33 mg/L).

In this case, a mixture with a concentration of C_0' was obtained from the known C_0 and the values of C_{e2} and F as determined by the requirements of the treatment, following the procedure in Section 2. To improve the accuracy of the CTA-MF calculation method, the isotherm with the initial concentration of C_0' was obtained through another jar test described in Section 3.2 because the value of C_0' was beyond the range of the RSM function. The results of the jar tests are shown in Fig. 5a and Table 3. In addition, the value of C_0' changed with that of C_0 , so it was assumed that the values of $K_{FO'}$ and $1/n_0'$ obtained from a particular concentration C_0' (25.79 mg/L) were applicable within that fluctuation range.

Furthermore, the value of C_{e1} was calculated by the CTA-MF calculation method. The adsorption isotherm experimental results with different initial concentrations of C_0 , C_0' and C_{e1} as described by DOC and COD are shown in Fig. 5.

As known conditions, the setting data and experimental results are shown in Table 3, which were then substituted into the CTA-MF calculation method together with Eq. (7) to calculate the PAC dosage and other parameters shown in Table 3 using the cut-and-try method. The calculated results of C_{e1} and C_{e2} were 17.51 mg/L and 9.320 mg/L, respectively, while the values of C_0 , x_1 and x_2 were 28.54 mg/L, 0.2600 g/L and 0.4800 g/L. The DOC concentration in MF effluent (<10 mg/L) could meet the requirements of SRO. If the conventional single stage adsorption process was adopted, the dosage of fresh PAC should be 0.7604 g/L to obtain an MF effluent with a DOC concentration of 9.320 mg/L.

To investigate the accuracy of the RSM function, the experimental isotherms with initial DOC and COD concentrations of 17.57 mg/L and 69.25 mg/L, respectively, were compared with the corresponding fitting isotherms obtained from the RSM functions. The results are shown in Fig. 6. The fitting isotherms from the RSM function coincided with the experimental results within the range of predetermined inflow concentration of SRO (a DOC value of approx. 9.000 mg/L, a COD value of approx. 45.00 mg/L). Therefore, adsorption isotherms with different initial concentrations can be well described by using RSM functions.

The changing trends of three fitting adsorption isotherms with different initial concentrations by RSM function shown in Fig. 6 were similar to those shown in Fig. 5. When the equilibrium concentration C_e was a constant, the amount of DOC adsorbed by the PAC was reduced with the decrease of the initial concentration in Figs. 5a and 6a. Thus, it

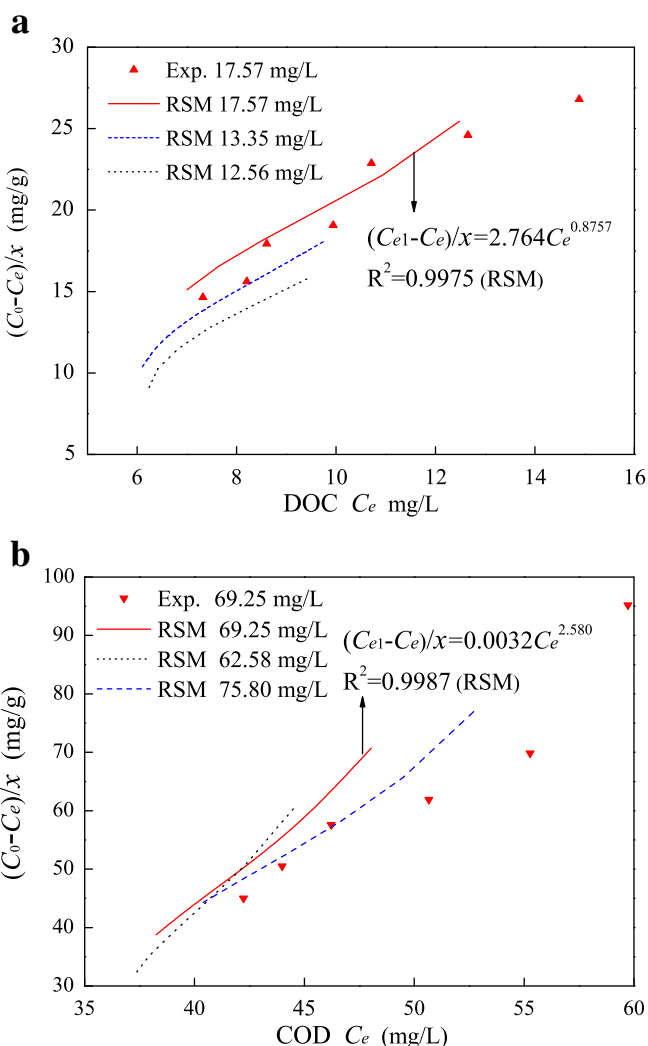


Fig. 6. The changing trends of RSM fitting isotherms, and the comparison of fitting isotherm with experimental results (DOC = 17.57 mg/L, COD = 69.25 mg/L) to prove the RSM function.

is necessary to study the initial concentration in order to predict the MF effluent quality through the CTA-MF calculation method. However, in Figs. 5b and 6b, the adsorption isotherms were close, and even crossed with different initial COD concentrations except for the isotherm of the primary ROC, which indicates that the amount of COD adsorbed by the PAC had been less affected by different initial concentrations. The above phenomenon was primarily due to competitive adsorption of the different organics. Therefore, it is very important to examine the effect of the initial adsorbate concentration on the adsorption isotherm in multi-component adsorption systems.

4.4. Verification of CTA-MF calculation method

In these experiments, the values of x_1 and x_2 were obtained from Section 4.3. The C_0 of the primary ROC described by the DOC or COD value was determined by experiments. These known parameters were substituted into Eqs. (4) and (5) to calculate the C_{e2} values of the MF effluent. In comparing the calculated and experimental results, the accuracy of the CTA-MF calculation method was verified. The experimental methods were previously referred to in Section 3.3; results are shown in Fig. 7.

In Fig. 7a, the DOC average values in the experiments decreased from 28.5 mg/L to 7.82 mg/L (the calculated value from CTA-MF calculation

Table 3
The experimental and calculated results of DOC for CTA-MF process.

Parameters	Setting data	Cal. results
F	0.1	/
C_{e2}	9.000	9.320
x_1	/	0.2600
x_2	/	0.4800
Parameters	Exp. results	Cal. results
C_0	28.54	/
C_0'	25.79	26.62
C_{e1}	17.57	17.51
K_{FO}	4.061	/
$1/n_0$	0.8191	/
$K_{FO'}$	4.878	/
$1/n_0'$	0.6981	/

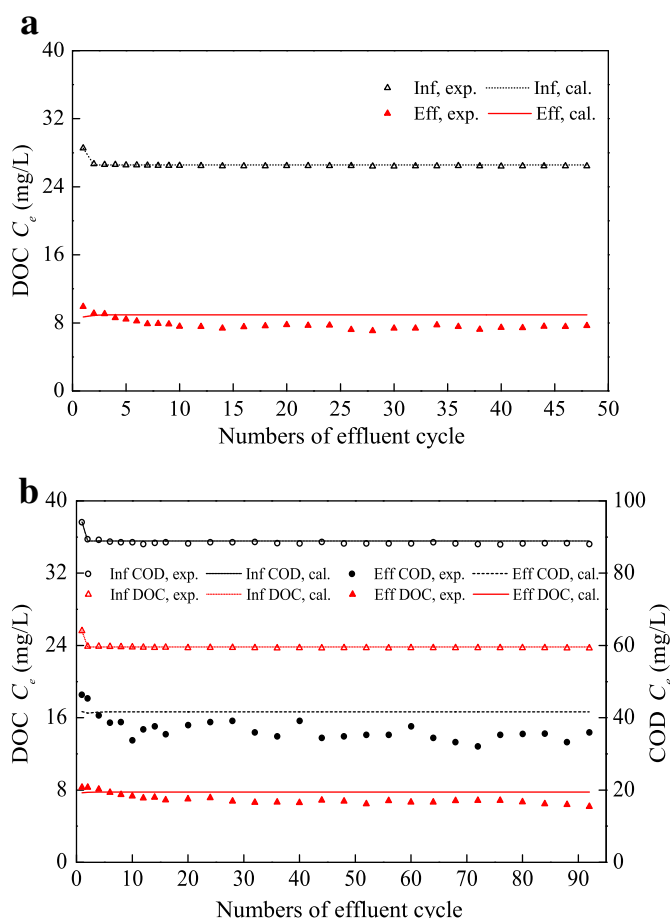


Fig. 7. The comparison of predicted values and the experimental results according to different ROCs at a certain PAC dosage ($x_1 = 0.26$ g/L, $x_2 = 0.48$ g/L). (a) DOC = 28.54 mg/L, COD = 107.5 mg/L; and (b) DOC = 25.61 mg/L, COD = 94.14 mg/L.

method was 8.96 mg/L); in Fig. 7b, the COD and DOC experimental average values decreased from 94.1 mg/L and 25.6 mg/L to 36.9 mg/L and 6.98 mg/L, respectively (the calculated values from CTA-MF calculation method were 39.2 mg/L and 8.00 mg/L). Therefore, the calculation method can properly calculate the dosage of PAC and satisfactorily predict the MF effluent within a small water quality fluctuation.

Observing the MF effluent concentration in Fig. 7, the initial experimental results were slightly higher than the calculated values due to the fresh PAC adhering to the inner wall of the reactor. The experimental results then slowly decreased with the subsequent values closer to the calculated ones within the first 10 MF effluent cycles. Afterwards, the experimental MF effluent quality was essentially stable and slightly lower than the calculated values because of the remaining adsorption amount of the loaded PAC that had been accumulated in the reactor. This phenomenon was also attributed to the adsorption of the PAC cake layer on the MF membrane surface, forming a microenvironment with a higher concentration of loaded PAC.

5. Conclusions

A hybrid process of CTA-MF was developed to remove the dissolved organics in petrochemical ROC with lower PAC dosage. Furthermore, a simple calculation method of CTA-MF process was established to

calculate the PAC dosage and predict the MF effluent quality based on the Freundlich equation, mass balance principle and RSM function.

When the fresh PAC dosage was 0.48 g/L, the removal rates of DOC and COD in ROC were 72.7% and 60.8%, respectively. Although there was a small fluctuation of DOC and COD in the ROC, the average difference of removal rates between the experiments and calculations were 3.75% and 6.09%, respectively.

The dissolved organics in ROC can be removed efficiently by CTA-MF process and predicted satisfactorily by the corresponding calculation method. A high overall recovery (91%) of RO could be achieved through reclaiming the treated ROC.

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