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Coking wastewater treatment for industrial reuse purpose: Combining biological processes with ultrafiltration, nanofiltration and reverse osmosis

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Abstract

A full-scale plant using anaerobic, anoxic and oxic processes (A_1/A_2/O), along with a pilot-scale membrane bioreactor (MBR), nanofiltration (NF) and reverse osmosis (RO) integrated system developed by Shanghai Baosteel Chemical Co. Ltd., was investigated to treat coking wastewater for industrial reuse over a period of one year. The removals reached 82.5% (COD), 89.6% (BOD), 99.8% (ammonium nitrogen), 99.9% (phenol), 44.6% (total cyanide (T-CN)), 99.7% (thiocyanide (SCN^-)) and 8.9% (fluoride), during the A_1/A_2/O biological treatment stage, and all parameters were further reduced by over 96.0%, except for fluoride (86.4%), in the final discharge effluent from the currently operating plant. The pilot-scale MBR process reduced the turbidity to less than 0.65 NTU, and most of the toxic organic compounds were degraded or intercepted by the A_1/A_2/O followed MBR processes. In addition, parameters including COD, T-CN, total nitrogen, fluoride, chloride ion, hardness and conductivity were significantly reduced by the NF-RO system to a level suitable for industrial reuse, with a total water production ratio of 70.7%. However, the concentrates from the NF and RO units were highly polluted and should be disposed of properly or further treated before being discharged.

Key words: coking wastewater; industrial water reuse; biological treatment; MBR; NF-RO

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Introduction

Pollution caused by coking wastewater is a serious problem all over the world, especially in China, where coal is one of the main energy sources for the iron and steel industry. Coking wastewater is usually generated from coal coking, coal gas purification and byproduct recovery processes. These processes consist of a high concentration of ammonia, toxic and carcinogenic substances, such as phenol, cyanide (CN^-), thiocyanide (SCN^-), polycyclic aromatic hydrocarbons (PAHs) and nitrogen-, oxygen- or sulfur-containing heterocyclic compounds (Ghose, 2002; Park et al., 2008). Therefore, it is necessary to treat coking wastewater properly to avoid any adverse long-term environmental and ecological impacts to the receiving water body.

Biological treatments, such as anoxic-oxic (A/O) or anaerobic-anoxic-oxic (A_1/A_2/O) processes, are widely applied in coking wastewater treatment because of the high treatment efficiency and cost-effective advantages (Vázquez et al., 2006; Qi et al., 2007; Sraib and Lant,

2007; Kim et al., 2008; Lai et al., 2008; Maranon et al., 2008; Li et al., 2010; Wang et al., 2012). Unfortunately, due to the refractory and inhibitory contaminants present in coking wastewater, the above processes are not sufficient in practice to meet the National Discharge Standard of China (GB8978-1996) or the stricter Shanghai Discharge Standard (DB31/199-2009) when accounting for criteria such as the chemical oxygen demand (COD), total cyanide (T-CN) and fluoride, among others (Wang et al., 2002; Park et al., 2008). To comply with the stringent environmental regulations, physico-chemical processes, such as coagulation or advanced oxidation, have to be involved following the biological process to ensure that the wastewater effluent approaches the local discharge standard (Chang et al., 2008; Lai et al., 2009; Ba and Li, 2012). However, a new revised regulation for accessory conditions in the coking industry was issued by the Ministry of Industry and Information Technology of the People's Republic of China in 2008 in which the production wastewater discharge from newly built coking plants is completely prohibited to result in zero discharge. Because wastewater is inevitably produced in coking plants, the only way for a new coking

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plant to achieve zero discharge targets is to internally reuse the wastewater.

To promote the reuse of coking wastewater for the water cooling system in Shanghai Baosteel Chemical Co. Ltd., the effluent quality from the coking wastewater treatment plant has to be improved to be consistent with the requirements of the National Standard of Water Quality for Industrial Use (GB/T19923-2005), in which COD $\leqslant$ 60 mg/L, SS $\leqslant$ 10 mg/L, total hardness $\leqslant$ 450 mg/L and Cl$^-\leqslant$ 250 mg/L, and the Criteria of Baosteel Industrial Water, in which COD $\leqslant$ 30 mg/L, total hardness $\leqslant$ 100 mg/L, Cl$^-\leqslant$ 60 mg/L and conductivity $\leqslant$ 500 μS/cm. It is clear that the limitations for this purpose are caused by the much more strict effluent criteria, such as COD, chloride ion and conductivity, among others. So far several studies have reported that combining a membrane bioreactor (MBR) with an $A_1/A_2/O$ system, i.e., $A_1/A_2/O$-MBR system, can effectively enhance the quality of coking wastewater effluent (Juang et al., 2007; Qin et al., 2007; Zhao et al., 2009a, 2009b). In addition, other membrane technologies, such as nanofiltration (NF) and reverse osmosis (RO), are increasingly applied as a separation technique in desalination, selective separation, and other chemical and environmental engineering fields (Lee et al., 2006; Pearce, 2008; Jacob et al., 2010; Dolar et al., 2011; Korzenowski et al., 2011). Specifically, NF is selected in front of RO unit due to its superior salt rejection function and the decrease of RO pressures associated to organic matters (Minhalma and Pinho, 2004), which have been also demonstrated by other researchers in separation of cyanide from coking wastewater by cross flow nanofiltration (Kumar et al., 2011) and separation of ammonium salts from coking wastewater with nanofiltration combined with diafiltration (Yin et al., 2011). Moreover, MBR can also strengthen organic removal further by keeping high concentration of biomass in reactor and therefore provide satisfactory pretreatment of wastewater for the subsequent NF and RO stages to further improve the quality of the effluent (Tam et al., 2007). Hence, it is anticipated that the combined $A_1/A_2/O$ process followed by MBR and NF-RO integrated system will be an attractive technique for treating coking wastewater for industrial reuse in Baosteel Company.

Therefore, the aims of this study are: (1) to thoroughly evaluate the performance of the current $A_1/A_2/O$ full-scale coking wastewater treatment plant operated by the Shanghai Baosteel Chemical Co. Ltd. in Shanghai, China; (2) to investigate the performance of a pilot-scale MBR and NF-RO integrated system for requirement of coking wastewater reuse; and (3) to assess the removal of toxic organic compounds in the $A_1/A_2/O$-MBR and NF-RO system by GC/MS analysis. To our best knowledge, this is the first study concerning full- and pilot-scale tests for coking wastewater treatment for the purpose of wastewater reuse.

1 Materials and methods

1.1 Coking wastewater

The characteristics of the raw coking wastewater from Shanghai Baosteel Chemical Co. Ltd. are listed in **Table 1**. Most parameters in the raw coking wastewater were tested in a whole year, in which COD, NH$_3$-N and T-CN were sampled nearly each day. Oil, phenol, SCN$^-$, fluoride and pH were analyzed 5 times per week, and biochemical oxygen demand (BOD), NO$_2^-$-N, NO$_3^-$-N, total nitrogen (TN) and total phosphorus (TP) once per week. The wastewater was deep brown in color with a bad odor and had highly fluctuating COD, phenol and ammonium nitrogen concentrations in the ranges of 940–2730, 18–290, and 93–790 mg/L, respectively. Moreover, the T-CN, SCN$^-$ and fluoride values in the raw coking wastewater were also significant.

1.2 Full-scale coking wastewater treatment plant

The industrial coking wastewater treatment plant in Shanghai Baosteel Chemical Co. Ltd. is currently operated for over 15 years by employing an $A_1/A_2/O$ biological system consisting of an anaerobic reactor (A_1, 1900 m^3, packed with semi-soft media that were constructed of plastic rings and synthetic fiber string) for anaerobic hydrolysis of refractory organic matters, an anoxic reactor (A_2, 6780 m^3, 2/3 of the volume is also packed with the same semi-soft media, and the left 1/3 is completely mixed by a submersible mixer) for denitrification, and an oxic reactor (O, 10,800 m^3, completely mixed by an air compressor) for biodegradable organic matter removal and nitrification (Phase I in **Fig. 1**). Activated sludge is returned from a sedimentation tank to the oxic reactor (1:1) to maintain the mixed liquor suspended solid (MLSS) concentration in the oxic reactor at approximately 4000 mg/L. The mixed effluent from the oxic reactor is returned to the anoxic reactor (3:1) for nitrogen removal by denitrification. The supernatant in the sedimentation tank is treated through a physico-chemical process by adding ferrous sulphate (FeSO$_4$), calcium chloride (CaCl$_2$) and polyaluminum

Table 1 Characteristics of raw coking wastewater

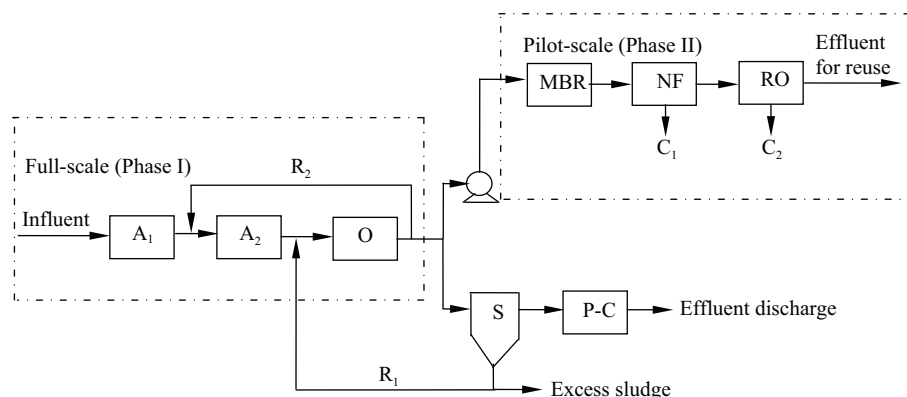| Parameter	Range	Mean ± SD	Number of measurement
COD (mg/L)	940–2730	1470 ± 286	341
BOD (mg/L)	186–462	298 ± 91	50
NH$_3$-N (mg/L)	93–790	215 ± 66	341
TN (mg/L)	212–298	251 ± 21	50
NO$_3$-N (mg/L)	9.9–18.2	13.5 ± 3.3	50
NO$_2$-N (mg/L)	0.01–0.1	0.05 ± 0.03	50
Oil (mg/L)	2.2–33.4	10.4 ± 3.9	242
Phenol (mg/L)	18–290	71 ± 40	242
T-CN (mg/L)	3.0–17.5	8.3 ± 2.6	341
SCN$^-$ (mg/L)	57–616	224 ± 67	241
Fluoride (mg/L)	22–72	45.0 ± 8.9	242
pH	8.7–9.3	9.0 ± 0.2	242
Total P (mg/L)	0.74–6.7	1.7 ± 1.1	50

Fig. 1 Schematic diagram of full- and pilot-scale setup. A_1: anaerobic, A_2: anoxic, O: oxic, S: settling tank, P-C: physico-chemical treatment, MBR: membrane bioreactor, NF: nanofiltration, RO: reverse osmosis, R_1: sludge reflux, R_2: wastewater reflux, C_1: NF concentrate, C_2: RO concentrate.

sulfate (PAS) coagulants to further reduce the fluoride, T-CN and COD levels to meet the wastewater discharge standard in Shanghai, China.

The coking wastewater treatment plant in the Baosteel Company was operated at 35–38°C, with an average flow rate of 200 m^3/hr. The pH in the oxic reactor was maintained at 6.5–6.8 by quantitatively dosing with Na_2CO_3 solution. Dissolved oxygen (DO) in the oxic reactor was maintained between 5–6 mg/L through the entire test period. The total hydraulic retention time (HRT) was 85 hr, with HRTs in the A_1, A_2, and O reactors of 8, 30, and 47 hr, respectively. The sludge retention time (SRT) in the oxic reactor was maintained at 50 days.

The samples were taken from A_1 effluent, A_2 effluent around 3 times/week, and O effluent and final discharge effluent around 5 times/week in the full-scale plant. The analytical parameters included COD, BOD, NH_3-N, NO_2^--N, NO_3^--N, TN, T-CN, SCN^-, fluoride and phenol, etc.

1.3 Pilot-scale test for the MBR and NF-RO integrated system

Pilot-scale facilities including the MBR and NF-RO integrated system were built to further investigate coking wastewater treatment (see Phase II in **Fig. 1**). Four modules consisting of flat-sheet submerged membranes (130 sheets of membrane with a total surface area of 195 m^2 in each module, pore size of 0.1 μm, and made of polyvinylidene fluoride material, Shanghai Sevoo, China) were installed in an MBR configuration (35 m^3 working volume). The effluent from the oxic reactor was pumped into the MBR, and the pilot-scale plant was operated at a flow rate of 10 m^3/hr. The DO level was maintained around 6.0 mg/L by compressed air under the membrane modules. The MLSS concentration in the MBR was maintained around 8500 mg/L, and the ratio of mixed liquor volatile suspended solids (MLVSS) to the MLSS was 0.78 in average. The HRT and SRT were kept at 3.5 hr and 90 days in MBR facility. The COD and turbidity data in the influent in MBR facility were analyzed using the supernatant of the samples

after 30 min of precipitation. The MBR effluent from each membrane module was drawn intermittently one by one by a suction pump (Chlf(T)12-10, Nanfang Pump Co. Ltd., Shanghai, China) at a constant rate with a filtration/idle cleaning ratio of 6 min:2 min. When the transmembrane pressure (TMP) reached 30 kPa, off-line physical cleaning (with tap water) and chemical cleaning (with HCl, NaOH and NaClO) were performed to restore the membrane flux.

The permeate from the MBR configuration was fed into the NF (GE, DK8040F1001, USA, feed pressure 0.6 MPa, membrane pore size around 0.001 μm, filtration time 2–3 months in one cycle) and RO (GE, Duraslick RO4040, USA, anti-fouling series, feed pressure 1.0 MPa, membrane pore size around 0.0001 μm, filtration time 2–3 months in one cycle) integrated system. The NF unit included three sets designed in series, and the RO had two sets in series. In the NF unit, the concentrate from the first set was fed into the second, and the concentrate from the second was fed into the third. The productive water from each set was collected together and fed to the RO unit. The RO unit also worked in series similar to the NF unit, and the productive water from the RO was collected for industrial reuse. The concentrates from both the NF and RO units (C_1 and C_2) were collected for disposal or further treatment.

The samples were taken from the MBR influent, MBR effluent (the same as NF influent), NF effluent and RO effluent around twice/week in the pilot-scale integrated MBR and NF-RO system. The analytical parameters included COD, TN, T-CN, fluoride, chloride ion, total hardness, conductivity and TDS, etc.

1.4 Analytical methods

The wastewater was analyzed for various parameters, including COD, BOD, NH_3-N, NO_2^--N, NO_3^--N, TN, T-CN, SCN^-, oil, TP, fluoride, chloride ion, phenol, and hardness according to the Water and Wastewater Analytical Methods (SEPA, 2006). The pH was recorded using a pH meter (PHB-2, Shanghai Sanxin Instrumental Company, Shanghai, China) and the DO using a DO

meter (JPB607, Shanghai Stech Company, Shanghai, China). The turbidity was measured using a turbidity meter (Hanna, HI93414, Italy), and the solution conductivity was measured with conductivity meter (Hanna, HI8733, Italy) according to the Standard Methods (APHA, 1992). The CHN composition in the viscose layer formed on the membrane surface was measured following the technical specification of Elemental Analyzer (Vario EL III, Germany). The silt density index (SDI) was tested by filtration using a 0.45 μm filter (Millipore Corporation, USA) and calculated based on the Standard Methods (APHA, 1992). Measurements of the above parameters were conducted in duplicate, and the mean values are reported. The relative errors of these measurements were less than 5%.

GC/MS (DSQ, Thermoelectron Corporation, USA) was used to analyze the organic compounds after pretreatment using solid phase micro-extraction (50/30 μm DVB/CAR/PDMS, Supelco Corporation, USA). An HP-5MS capillary column with an inner diameter of 0.25 mm and a length of 30 m was adopted for the separation system. The temperature in the oven was maintained at 300°C. The temperature control program was set as 60°C for 2 min followed by an increase to 300°C at a rate of 20°C/min. The electron energy was set at 70 eV. Organic compound

analysis was undertaken with reference to the NIST mass spectral library database.

2 Results and discussion

2.1 Performance of the full-scale coking wastewater treatment plant

The coking wastewater treatment plant in Shanghai Baosteel Chemical Co. Ltd. employed $A_1/A_2/O$ biological treatment process followed by the physico-chemical treatment units as a polishing stage. The plant was carefully monitored over one year. The changes of the main parameters including COD, NH_3-N, phenol and T-CN are shown in **Fig. 2**, and the data displayed in mean values with other parameters such as BOD, NO_2^--N, NO_3^--N, fluoride and pH together in various stages are shown in **Table 2**.

In the $A_1/A_2/O$ system, though anaerobic reactor removed < 5% of the COD, the biodegradable part of organic matters increased as shown by the elevation of BOD/COD ratio from 0.20 to 0.27, suggesting that the anaerobic reactor played an important role in converting refractory or inhibitory compounds into biodegradable organic substances (Lai et al., 2008; Zhao et al., 2009a).
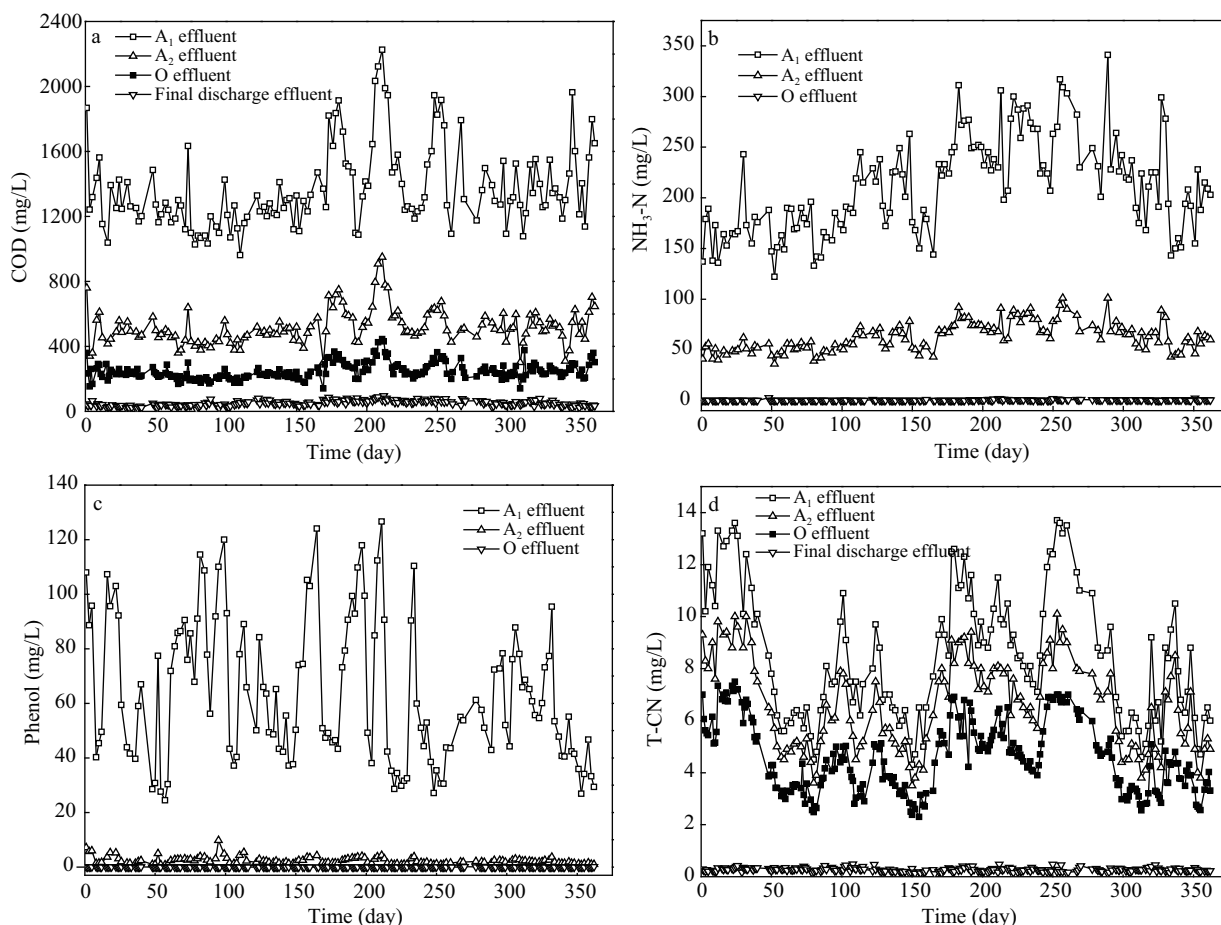

Fig. 2 Changes of COD (a), NH_3-N (b), phenol (c), and T-CN (d) in A_1 effluent, A_2 effluent, O effluent and final discharge effluent versus operational time.

Table 2   Performance of coking wastewater treatment plant

Parameter	A_1 effluent[a]	A_2 effluent[a]	O effluent[a]	Removal (%)	Final discharge effluent[a]	Total removal (%)
COD (mg/L)	1400 ± 250	548 ± 85	256 ± 73	82.5	50.3 ± 16.0	96.6
BOD (mg/L)	377 ± 62	71 ± 16	31 ± 19	89.6	12.0 ± 3.0	96.0
NH_3-N (mg/L)	225 ± 50	67 ± 14	0.41 ± 0.30	99.8	0.22 ± 0.10	99.9
NO_3-N (mg/L)	13.5 ± 3.5	4.8 ± 5.0	102 ± 27	/[b]	101 ± 27	/
NO_2-N (mg/L)	0.05 ± 0.03	1.8 ± 1.5	0.06 ± 0.03	/	0.06 ± 0.03	/
Phenol (mg/L)	70 ± 35	2.4 ± 1.0	0.02 ± 0.01	99.9	0.02 ± 0.01	99.9
T-CN (mg/L)	8.3 ± 3.0	6.7 ± 2.5	4.6 ± 1.4	44.6	0.26 ± 0.07	96.9
SCN^- (mg/L)	212 ± 58	27.3 ± 4.2	0.7 ± 0.1	99.7	0.68 ± 0.1	99.7
Fluoride (mg/L)	45.0 ± 9.0	42.0 ± 7.0	41.0 ± 7.0	8.9	6.1 ± 2.1	86.4
pH	8.7 ± 0.2	8.6 ± 0.2	7.1 ± 0.3	/	7.1 ± 0.4	/

[a] Data are present as mean ± standard deviation; [b] not available.

After the whole A_1/A_2/O biological treatment, COD and BOD removals reached 82.5% and 89.6% respectively (**Table 2**), and most of the COD removal achieved in the anoxic and oxic reactors was due to the oxidation of the biodegradable organic substances in the oxic reactor, and the requirements of organic materials by microorganisms in the anoxic reactor during denitrification. Our results were consistent to some lab-scale test and pilot-scale test results where employing biological processes for coking wastewater treatment. For instance, Zhao et al. (2009a) showed that 83.5% COD removal efficiency could be reached when treating coking wastewater by A_1/A_2/O system in their lab-scale test, and around 81% COD removal could be achieved when treating coal gasification wastewater using lab-scale moving bed biofilm reactor by Li et al. (2011). In addition, Maranon et al. (2008) observed that around 85% COD could be removed when treating coke wastewater in a sequential batch reactor (SBR) at a pilot-scale plant. However, the COD value after biological treatment was still higher in the full-scale plant than the required discharge standard (< 100 mg/L) and most residual COD were composed of refractory or non-biodegradable matters (BOD/COD = 0.12). Fortunately, the final polishing stage using the physico-chemical treatment reduced the COD to approximately 50.3 mg/L, which was much less than the target values for wastewater discharge (**Fig. 2a**).

In contrast, ammonium nitrogen was easily oxidized and almost completely converted into nitrate in the oxic reactor (**Fig. 2b**). Through denitrification, part of the nitrate was converted into nitrogen gas. Phenol was completely removed because it was readily oxidized in the oxic reactor (**Fig. 2c**), whereas SCN^- was also completely oxidized in the oxic reactor (**Table 2**). Vazquez confirmed that 98% of phenol and 90% of SCN^- could be removed in aerobic reactor in a lab-scale coking wastewater treatment test (Vázquez et al., 2006). While Kim demonstrated that nearly 100% of phenol, free cyanide and SCN^- in coking wastewater could be removed when applying pre-denitrification process in a lab-scale serial anoxic-aerobic reactor (Kim et al., 2008). Unfortunately, only 44.6% of T-CN was removed after biological treatment which was due

to the part existence of complex cyanide form in coking wastewater (**Fig. 2d**) and, at the same time, only 8.9% of fluoride was removed after biological treatment. Therefore, at the polishing stage, $FeSO_4$ was added at pH 4.5–4.8 to form ferric cyanide ($Fe(CN)_6^{3-}$); $CaCl_2$ was added at pH 7.0 to form CaF_2; and PAS was added as a coagulant. After the final sedimentation, most of the T-CN and fluoride was removed, with the final average concentrations in effluent at 0.26 and 6.1 mg/L, respectively, thereby satisfying the Shanghai Discharge Standard (T-CN < 0.3 mg/L, fluoride < 10 mg/L).

It should be noted, from the above results, that satisfactory performance was maintained over the entire monitoring period in the present coking wastewater treatment plant, and the effluent after the post-treatment stage complied with the local wastewater discharge standard. However, for the purpose of wastewater reuse as cooling water in the Baosteel Company, the criteria for COD, chloride ion, and conductivity, among other factors, did not meet the requirements. Therefore, further treatment by employing the MBR and NF-RO integrated system was investigated and its performances are discussed in the following sections.

2.2 Performance of the MBR system

The MBR system was investigated for more than one year coinciding with the full-scale plant monitoring period. The HRT was maintained at 3.5 hr, and the MLSS in the MBR was kept at approximately 8500 mg/L during the entire test period. The MBR performances for one MBR running cycle (120 days) between membrane cleaning are shown in **Fig. 3**. It was clear that the influent COD fluctuated between 172 and 301 mg/L due to the variation of wastewater qualities during the production period, whereas the effluent COD ranged from 137 to 243 mg/L (**Fig. 3a**), indicating around 19.2% of COD was removed further after the MBR treatment. Because most of the biodegradable organic matter had already been removed in Phase I (BOD = 31 mg/L, COD = 256 mg/L, BOD/COD = 0.12 in effluent of phase I), a large quantity of organic matters in influent for the MBR system was refractory or non-biodegradable. It was assumed that some refractory
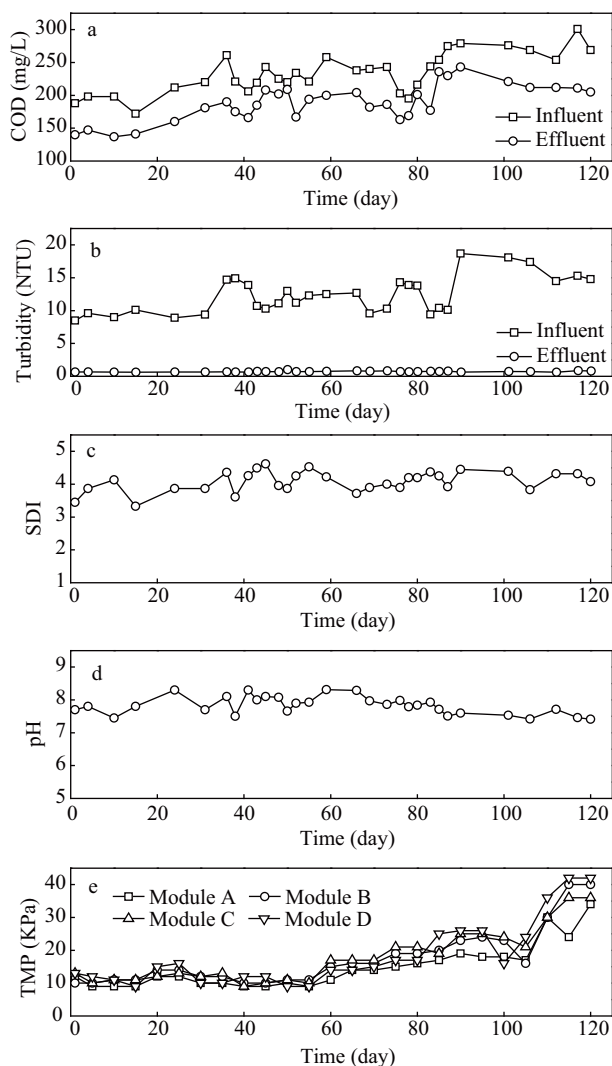
Fig. 3   Performances of MBR process of (a) COD, (b) turbidity, (c) effluent SDI, (d) effluent pH, (e) transmembrane pressure (TMP).

organic parts might also be degraded because of the higher biomass concentration remained in MBR facility. Whereas the removed COD in the MBR system was also probably due to membrane filtration as well as the interception function through the viscose film formed on the membrane surface. Zhao has already demonstrated that employing MBR following $A_1/A_2/O$ process was more efficient and reliable in pollutants and acute toxicity reduction than the conventional $A_1/A_2/O$ system in coking wastewater treatment, and this advantage was owed to the creation of a low food to microorganism environment to strengthen refractory substances degradation and reduce sludge production rates (Zhao et al., 2009a, 2009b). In addition, even the turbidity fed into the MBR system varied significantly (8.5–18.7 NTU) caused by the water quality variation in influent of the full-scale coking wastewater treatment plant, the effluent from the MBR always produced high quality of treated water with a turbidity of approximately 0.56 NTU

in average (**Fig. 3b**), showing a great advantage of using MBR to keep suspended solids and colloidal materials away from the effluent after membrane filtration, which would be beneficial for further NF and RO treatments. Moreover, the results of the silt density index (SDI) test (SDI < 5.0) also suggested that the MBR effluent was acceptable as the influent for the NF or RO systems due to the lower potential for membrane fouling (**Fig. 3c**). Furthermore, the pH in the MBR effluent varied between 7.4 and 8.3, with a mean pH value of 7.8, which was within the range suitable for NF or RO treatment (**Fig. 3d**). It should be noted that MBR facility was separated in this pilot-scale test in order not to affect the full-plant operation. However, in the practical design of this process it might be reasonable to put MBR module directly into the oxic tank to save the necessarily occupied area.

Membrane fouling was also investigated with long-term monitoring of the MBR system for the entire test period. Four pressure gauges were set in the export of each membrane module, at the same location as the suction pump import. The changes in TMP for each membrane module during one MBR running cycle are shown in **Fig. 3e**. During the initial 57 days of operation, the TMP for the four modules were steady. From 58 to 106 days, the TMP increased slightly, and it increased remarkably during the final 14 days. As a result, the flow rate could not be maintained to meet the demand for the subsequent NF-RO system; therefore, it was necessary to clean the membranes.

A viscose layer formed on the membrane surface was the main reason for the decrease in the membrane flux. It has been reported that the organic matter that accumulated in the MBR supernatant by the colloidal organic fraction caused membrane fouling, in which polysaccharides and proteins derived from soluble microbial products through microbial metabolisms contributed significantly (Zhao et al., 2010). To investigate the composition of the viscose layer in this study, the deposit sample of the viscose layer was collected from the membrane surface before membrane cleaning and dried at 105°C. The CHN elemental analyses showed that carbon, hydrogen and nitrogen contributed 48%, 4.0% and 7.7%, respectively. The 82% loss after the deposit ignition test at 925°C for one hour also suggested that the viscose layer was mainly composed of organics. In addition, the elemental analyses by X-ray fluorescence indicated that 18% of the deposit was inorganic matter, including sulfur (SO_3), iron (Fe_2O_3), sodium (Na_2O), calcium (CaO), chlorine and phosphorus at 5%, 2%, 2%, 1%, 1% and 1%, respectively. Nevertheless, after four cycle tests for over one year, the membrane cleaning procedure, which consisted of physical washing using tap water and submerged cleaning by chemicals, showed a significant removal of the deposit on the membrane surface and a great recovery of membrane flux (data not shown).

2.3 Performance of the NF-RO system

Even though the MBR system successfully removed suspended solids and most of the colloidal organic matter, it failed to remove the dissolved salts and was not able to reduce the COD to a level for wastewater reuse in industry, especially when parameters such as COD, total hardness, chloride ion and conductivity were taken into account. Therefore, further treatment by employing a NF-RO integrated system was investigated in pilot-scale test. The NF-RO system was operated for over one year, and the performances of the NF and RO units in one running cycle period are shown in **Fig. 4**, while the data along with other parameters displayed in mean values are shown in **Table 3**. Apparently, COD was significantly reduced through the NF unit (90.6% removal efficiency in average), showing a great advantage of NF unit in organic matters removal, and was maintained at approximately 7.0 mg/L after the RO unit which is much less than 30 mg/L required for industrial reuse in the Baosteel Company (**Fig. 4a**). In addition, T-CN was almost completely rejected in the NF-RO system (**Fig. 4c**). Though the solution conductivity entering the NF unit changed remarkably (5100–8080 μS/cm), the values from the RO effluent were very stable (< 500 μS/cm). Both the NF and RO units reduced the solution conductivity, with the NF and RO contributing

Fig. 4   Performances of NF-RO units in one operational cycle (a) COD, (b) fluoride, (c) T-CN, (d) conductivity.

Table 3   Performance of NF and RO system

Parameter	NF influent[a]	NF effluent[a]	Removal (%)	RO effluent[a]	Removal[b] (%)	Total removal (%)
COD (mg/L)	191 ± 61	18.0 ± 6.0	90.6	7.0 ± 4.3	5.7	96.3
TN (mg/L)	119 ± 29	120 ± 25	−0.8	16.5 ± 13	87.0	86.1
T-CN (mg/L)	4.1 ± 1.3	0.5 ± 0.3	87.8	0.002 ± 0.001	12.1	100
Fluoride (mg/L)	41 ± 7.0	29.0 ± 1.9	29.3	2.5 ± 2.0	64.6	93.9
Conductivity (μS/cm)	6940 ± 632	4700 ± 640	32.2	299 ± 85	63.5	95.7
Total hardness (mg/L)	71.8 ± 14.0	21 ± 15	70.8	5.0 ± 0.5	22.3	93.1
Chloride ion (mg/L)	837 ± 157	859 ± 93	−2.6	38.6 ± 15.0	98.0	95.4
SiO$_2$ (mg/L)	10.7 ± 11.0	8.4 ± 5.0	22.2	5.7 ± 2.3	25.0	47.2
TDS (mg/L)	3770 ± 546	2240 ± 638	40.8	271 ± 155	52.0	92.8

[a] Data are presented as mean ± standard deviation; [b] RO removal = (NF effluent – RO effluent)/NF influent.

to 32.2% and 63.5%, respectively, with a total reduction of 95.7% (**Fig. 4d**). Hardness, including both Ca- and Mg-hardness, was significantly removed by the NF unit (70.8%), which is benefit remarkably to the process since this can avoid the formation of CaF precipitation in the followed RO unit. Though NF could not reject any chloride ion and, in contrast, chloride ion concentration increased in NF effluent slightly due to the addition of less amount of NaClO in MBR effluent (5–10 mg/L) for antibiotic action in protection of the followed NF-RO units, RO worked very well in regard to chloride ion removal. The same as chloride ion, total nitrogen could not be removed by NF unit but by RO unit (**Table 3**). In addition, the amount of total dissolved salt (TDS) was greatly reduced in the NF-RO system (92.8%), with NF and RO contributing to 40.8% and 52.0%, respectively. From above results it can be concluded that only employing both NF and RO units can treated water satisfy the requirement for Baosteel industrial water reuse quality, in which NF unit contributed most to COD, T-CN and total hardness removals and RO to TN, fluoride, conductivity, chloride ion and TDS removals. To the authors best knowledge, even NF or RO units are widely applied in sea water desalination, reclaimed water from domestic wastewater, or salt separation of dissolved solids in various industrial fields, there are less application in purpose for coking wastewater reuse though there are some lab-scale tests for cyanide separation or ammonium salts separation from coke wastewater by NF (Kumar et al., 2011; Yin et al., 2011). The NF-RO system normally could work 2–3 months in one cycle and then need to be washed when the water productive ratio dropped around 15% or the filtration pressure dropped around 15%. During the entire operation of the NF-RO system, the water production ratios were 85.9% and 82.4% for the NF and RO units, respectively, with a total production ratio of 70.7% (**Fig. 5**), representing a satisfactory result. Moreover, it was estimated that the cost for water production through this integrated full-scale $A_1/A_2/O$ plant and pilot-scale MBR and NF-RO systems would be elevated around 2.6 CNY/ton including electricity and chemical reagents consumptions, which is
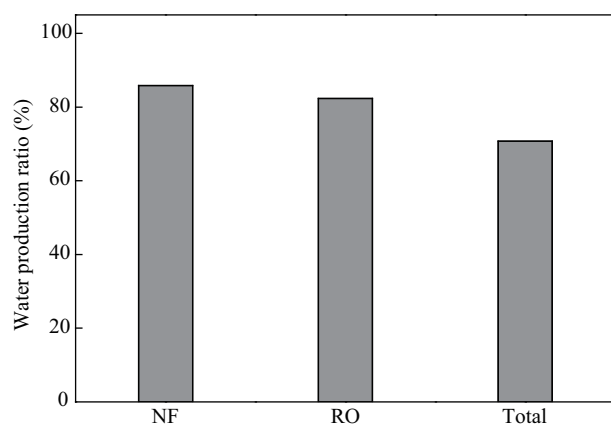
reasonable for plant operation.

The flow rates of concentrates from the NF and RO units were 1.4 and 1.5 m^3/hr, respectively, and their characteristics were also analyzed (**Table 4**). Compared with the permeate, the COD and T-CN mostly accumulated in the concentrate of the NF unit, and TN and chloride ions accumulated in the concentrate of the RO unit. Both concentrates from the NF and RO units had higher fluoride and TN contents, as well as much higher conductivities. It is obvious that the concentrates were highly polluted and could not be disposed of without proper treatment; this will be focus of our future work.

2.4 Biodegradation of toxic organic compounds in the whole system

To further investigate the performance of the entire process on the removal of toxic organic compounds in coking wastewater under normal testing conditions, GC/MS analysis was performed, and the results are displayed in **Table 5**. The organic compounds in the raw coking wastewater were shown to be very complex and included phenol, naphthalene, benzene and aniline as the main substances (in parts per million). Other organic substances also existed, including benzo[b]thiophene, acenaphthylene, acenaphthene, indene, indole, and quinoline, among others. After biological treatment in $A_1/A_2/O$ process, phenol and aniline were completely removed, and most of the naphthalene were degraded to parts per billion levels. Some new organic compounds were also detected as intermediates or byproducts in the oxic reactor effluent in the parts per billion range, and nearly all of the organic compounds were removed after MBR treatment, except for toluene, phthalic acid diisobutyl ester, dibutyl phthalate, and nonanal, suggesting that the $A_1/A_2/O$-MBR system was highly capable of removing toxic organic compounds (Li et al., 2003). However, no organic compounds were detected in the NF and RO production waters (data not shown). Therefore, it can be concluded that the production water from the NF-RO system to be reused for cooling water was environmentally friendly because none of the large and complicated molecular organic compounds were present.

Through the full-scale $A_1/A_2/O$ followed by the pilot-scale MBR and NF-RO process tests, it should be noted that the whole treatment plant facilitated a long process

Fig. 5 Water production ratio in Phase II.

Table 4 Analytical results of NF and RO concentrates

Parameter	NF concentrate	RO concentrate
Flow rate (m^3/hr)	1.4	1.5
COD (mg/L)	797 ± 212	102 ± 89
TN (mg/L)	111 ± 18	504 ± 174
T-CN (mg/L)	23.5 ± 10.0	0.23 ± 0.10
Fluoride (mg/L)	99.1 ± 31.0	115.2 ± 44.0
Chloride ion (mg/L)	670 ± 205	3160 ± 863
Conductivity (μS/cm)	14500 ± 2334	13670 ± 2527

Data are expressed as mean ± SD.

Table 5　Main organic compound analyses in the whole process

Organic compound	Raw water (mg/L)	Phase I effluent (μg/L)	MBR effluent (μg/L)	Organic compound	Raw water (mg/L	Phase I effluent (μg/L)	MBR effluent (μg/L)
Phenol	10.4	–	–	3-Methyl-benzothiophene	–	0.94	–
2-Methyl phenol	1.88	–	–	2-Methyl benzo[b]thiophene	–	0.21	–
4-Methyl phenol	3.75	–	–	Thionaphthene	–	0.66	–
2,4-Dimethyl phenol	0.29	–	–	Indane	–	0.14	–
2,5-Dimethyl phenol	0.88	–	–	Fluorene	0.16	0.42	–
Naphthalene	3.34	14.5	–	Benzofuran	0.12	–	–
1-Methyl-naphthalene	3.4	25.1	–	Dibenzofuran	0.09	0.9	–
2-Methyl-naphthalene	2.83	23.4	–	Pyridine	0.23	–	–
1,7-Dimethyl-naphthalene	0.34	0.64	–	2-Methyl-pyridine	0.31	–	–
2-Ethyl-naphthalene	0.28	2.17	–	Phthalic acid diisobutyl ester	0.01	0.8	0.39
2,6-Dimethyl-aphthalene	0.23	2.19	–	Dibutyl phthalate	0.01	3.84	2.75
2,7-Dimethyl-naphthalene	–	3.04	–	Acenaphthylene	0.81	1.34	–
1,4-Dimethyl-naphthalene	–	2.14	–	Anthracene	0.01	0.31	–
2-Ethyl-naphthalene	0.28	1.72	–	Acenaphthene	0.88	–	–
Benzene	0.14	–	–	Indene	0.71	–	–
Toluene	2.10	0.47	0.63	Indole	3.10	–	–
Biphenyl	1.28	12.4	–	Quinoline	1.12	–	–
1-Ethynyl-4-methyl-benzene	–	0.38	–	Benzonitrile	0.16	–	–
6-Methyl benzo[b]thiophene	1.11	–	–	Aniline	10.4	–	–
Benzo[b]thiophene	0.64	–	–	Nonanal	–	0.33	0.33

–: not detected.

compared with other wastewater treatment process aiming to wastewater reuse. This was significantly caused by the complex constituents in the raw coking wastewater and the strictly required standards for industrial reuse. However, this test strongly suggested that it is worthy to employ each unit in it in achieving refractory organics and nitrogen removals, lowing cyanide and fluoride contents and water conductivity, and maintaining long-term good performance, maintenance and operation of the facilities based on the zero-discharge philosophy in Baosteel Company, therefore showing a great potential in its application in future.

3 Conclusions

A full-scale plant using $A_1/A_2/O$, along with a pilot-scale MBR and NF-RO integrated system in Shanghai Baosteel Chemical Co. Ltd., was investigated to treat coking wastewater for industrial reuse. The current plant employed anaerobic-anoxic-oxic and physico-chemical processes and was effective at reducing the COD, ammonium nitrogen, phenol, T-CN, SCN^- and fluoride concentrations, but the effluent did not satisfy the requirement for industrial reuse because the COD, hardness, chloride ion, and conductivity, among others, were still too high. By combining an MBR into the $A_1/A_2/O$ system, around 19.2% of COD was further reduced, and the turbidity in effluent was completely removed. SDI results also showed a great advantage in employing the MBR as a pretreatment followed by the NF-RO system. Moreover, parameters including COD, T-CN, TN, fluoride, chloride ion and conductivity were significantly reduced by the NF-RO system to a level suitable for industrial reuse, and

most of the toxic organic compounds were degraded or intercepted by the $A_1/A_2/O$-MBR. Furthermore, none of complex or toxic organic compounds were detected in the NF and RO production waters, strongly suggesting the efficacy and effectiveness of the proposed process. However, the concentrates from the NF and RO units are highly polluted and should be disposed of properly or be further treated before discharge.

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