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Feasibility evaluation of the treatment and recycling of shale gas produced water: a case study of the first shale gas field in the Eastern Sichuan Basin, China†

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A cost-effective shale gas produced water (PW) treatment plant is an essential facility for safe wastewater management in the shale gas field in the Eastern Sichuan Basin, which is the first commercial shale gas field in China. However, knowledge on PW characteristics and disposal features of this developing shale gas field is limited. This study evaluated the feasibility of pollutant removal from PW in the Eastern Sichuan Basin by a sequential physicochemical process through laboratory and on-site pilot-scale experiments. The results indicated that the COD_{Cr}, ammonia nitrogen, total nitrogen, and total phosphorus in the PW are efficiently removed by Fenton–NaClO oxidation, multi-media filtration, and reverse osmosis (RO) processes. A novel recycling route was introduced to rationally dispose the RO concentrate, which was recycled as a raw brine material for a chlor-alkali enterprise through a physicochemical advanced treatment process. A laboratory-scale co-treatment of PW with domestic wastewater was also conducted. Salinity fluctuation, chemical pre-treatment toxicity, resistance, and resilience of the bioreactor after fluctuations may heavily influence the planning, design, and construction of a PW treatment plant, although a coupled chemical–biological process for treating PW is a potential cost-effective management technique. Overall, the sequential physicochemical process that includes RO is a feasible process for the cost-effective treatment of PW from the shale gas field in the Eastern Sichuan Basin. The recycling of the RO concentrate as a raw brine material for the chlor-alkali enterprise is a potential and novel resource recycling mode. The detailed results derived from this study will be considered as a reference for developing the first full-scale centralized shale gas PW treatment plant in this field.

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Water impact

Hydraulic fracturing technology has been successfully applied and vigorously promoted in China. However, flowback and produced water have gained new environmental concerns and have required special treatments before final disposal or reuse. Knowledge on the characteristics and disposal feasibility of produced water in the first shale gas field in the Eastern Sichuan Basin, China, is limited, and challenges in implementing a cost-efficient technology in the treatment practice exist. We evaluated the feasibility of pollutant removal and desalination from produced water by a sequential physicochemical process through laboratory and on-site pilot-scale experiments. This paper is the first systematic report on produced water management in a shale gas field in China.

Introduction

The immense success of exploration and commercialization of shale gas in the USA over the past two decades has shown considerable progress in energy revolution and gained great concerns around the world.[1–3] In China, shale gas has been commercially developed as an important unconventional natural gas resource since 2013.[14] Although a bright prospect for developing shale gas industry has been demonstrated, complaints have been raised about the potential negative impacts of hydraulic fracturing on environmental quality and human health.[5–7] The generally used hydraulic fracturing technology,

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which has enabled large-scale commercial development of shale gas coupled with horizontal drilling, has been applied extensively.[8] Large volumes of freshwater mixed with sand and other chemicals are injected into wells under high pressure during the fracturing process to create fractures in low-permeability shale formations.[8] At the early stage, that is, within the first 30 days, approximately 15–25% of water that returns to the surface is called flowback water, and the water that continues to flow for the entire life of the wells at a reduced rate is referred to as produced water (PW). Such wastewater mainly contains extremely complex dissolved chemicals, hydrocarbons, heavy metals, naturally occurring radioactive material (NORM), bacteria and water-soluble salts (such as potassium, calcium, sodium, carbonate, and chloride), thereby gaining increasing environmental concerns and requiring special treatment before final disposal or reuse.[9–12]

Implementing cost-effective PW management is one of the most important issues during the entire life cycle of shale gas fields.[13,14] To date, four PW disposal patterns have been implemented, namely, (1) underground injection, (2) reuse for subsequent hydraulic fracturing, (3) co-treatment with sewage in municipal wastewater treatment plants (WWTPs), and (4) centralized treatment in private industrial WWTPs in shale gas fields.[14,15] The technical feasibility of underground injection (option 1) is hampered in the shale gas field under delicate geological conditions and developed groundwater ecosystems.[4,13,16] Reusing PW for continuous hydraulic fracturing (option 2) is merely a temporary choice before the end of well drilling.[13] Furthermore, transporting PW to nearby municipal WWTPs for co-treatment (option 3) may result in salt accumulation in the sediments downstream of the plant and cause unstable operational performance of the biological treatment units.[14] On the basis of previous practical experience, PW management strategies tend to change from wastewater disposal to treatment to satisfy rapidly upgrading environmental requirements. Therefore, transporting PW into private industrial WWTPs for centralized treatment (option 4) has been considered as the optimum choice in view of sustainable shale gas environment management.[13,16,17]

Although a number of studies have examined the effectiveness of independent technology for removing partial contaminants or TDS from PW,[17–26] studies on the feasibility of an integral treatment process in private centralized shale gas PW treatment plants are limited.[13,17,18] Particularly, the efficiency and capacity of each technical unit in the treatment process, the capital investments and operational costs of the entire treatment process, and the effluent standard, as well as environmental risk control status, are urgently needed to guide the practical engineering design and implementation, especially in China.[27] As a rule, the applied wastewater treatment processes in the oil & gas industry for pollutant reduction of conventional PW can serve as models or references for establishing a feasible shale gas PW treatment process.[18] Generally, an integral PW treatment process in the conventional onshore oil & gas industry for a high-grade discharge level usually contains phase separation (*e.g.*, oil–water and solid–liquid separation), physicochemical primary pre-treatment (*e.g.*, coagulation), biological treatment (*e.g.*, aeration tank), secondary pre-treatment (*e.g.*, air flotation), membrane filtration (*e.g.*, ultrafiltration, nanofiltration, and reverse osmosis), and post-treatment (*e.g.*, softening).[18,28–31] The techniques for each treatment phase are varied.[32,33] Consequently, the shale gas PW combined treatment process of a centralized private industrial WWTP can be proposed after independent technique optimization when the TDS of the shale gas PW is below the limitation of pressure-driven membrane technology.[27,34]

Nevertheless, in addition to the well-investigated conventional oil & gas PW, the shale gas PW usually contains more salts and complex pollutants. Therefore, novel independent technologies, such as innovative desalination and advanced oxidation processes (AOPs), are being tested for the advanced removal of certain group components to meet increasingly strict environmental regulations.[13,17,18] Among them, innovative membrane-based technologies (*e.g.*, forward osmosis (FO)[20] and membrane distillation (MD)[21]), combined AOPs (*e.g.*, catalyzed ozone[22] and photo-Fenton process[23]), advanced thermal technologies,[24] and microbial capacitive desalination technique[25,26] have been successfully implemented in bench-or pilot-scale research. However, mature and emerging techniques should be evaluated as constituent parts in a proposed cost-effective treatment process to satisfy technical and environmental criteria.

The Eastern Sichuan Basin is the first commercialized large-scale shale gas field, which is a typical Lower Silurian Longmaxi marine shale gas block with an estimated reserve of 1067.5 billion m^3. Since 2016, this shale gas field has accumulated 12.23 billion m^3 of natural gas production and provided a bright prospect for developing unconventional natural gas in China. The development of centralized private industrial WWTPs for PW treatment and reuse is an important supporting project for the scaling-up of the shale gas field. Our team was authorized and financed by Sinopec in 2015 to conduct laboratory and on-site pilot-scale experiments to access the feasibility of the combined PW treatment and reuse processes. The technical reliability and operational cost of the integral process in the proposed full-scale plants were determined in detail. To the best of our knowledge, our study is the first systematic report on actual PW treatment and reuse by a combined process in China. The results of this study could pave the way for optimizing the PW treatment process in centralized private industrial WWTPs.

Materials and methods

PW samples

The PW referred to in this study is the freshly stored wastewater tank in the finished shale gas well station, which has been devoted to commercial production for 1 year. PW samples from 15 wells in the shale gas field of the Eastern Sichuan Basin in 2015 were collected, shipped to the laboratory, and stored at 4 °C in the dark prior to detailed pollutant measurements. The PW from one of the wells, which was represented as an influent for the planning-centralized shale gas PW treatment plant, was periodically collected and used for laboratory-scale experiments.

Experimental setup and procedure

(1) PW treatment for discharge: laboratory and on-site pilot-scale physicochemical pre-treatment–reverse osmosis (RO) process. Desalination is a crucial step for the effective treatment or reuse of PW. To date, emerging desalination processes, such as FO, MD, mechanical vapor compression, humidification–dehumidification, and pervaporation, have gained increasing popularity in comparison with traditional pressure-driven membrane processes.[13] However, RO still provides the best energy efficiency for desalination when the salinity of the saline wastewater is below the oceanographic range.[34] Therefore, regarding the salinity of the PW (26 g L^{-1}), RO was selected as the core desalination technique in this study. A sequential Fenton–NaClO oxidation combined with multi-media filtration was designed for eliminating suspended and dissolved solids, colloids, and organic and inorganic compounds to realize a low degree of membrane fouling (Fig. 1). Laboratory and on-site pilot-scale experiments were conducted. The detailed operational parameters for the laboratory-scale experiments are summarized in Table S1.† For the pilot-scale experiments, a 5 m^3 d^{-1} sequential advanced oxidation and RO process device was established near a typical well in the shale gas field in the Eastern Sichuan Basin. The process operational performance was optimized and compared with the obtained laboratory-scale results.

(2) PW RO concentrate treatment for external reuse: laboratory-scale of the sequential physicochemical process. A homologous sequential physicochemical process was designed to recycle RO concentrates as crude brine materials for a chlor-alkali factory, which is near the planning-centralized PW treatment plant in the shale gas field in the Eastern Sichuan Basin (Fig. 1). Detailed operational parameters for the laboratory-scale experiment of RO reuse are summarized in Table S2.†

(3) PW biological co-treatment with sewage in WWTPs: laboratory-scale of a sequential chemical pre-treatment–biological process. A sequential chemical–biological process was established to evaluate the treatability of PW biologically to save disposal cost (Fig. S1†). The same Fenton–NaClO oxidation was chosen as the chemical pre-treatment approach. A moving-bed biofilm reactor (MBBR) process was selected as the biological treatment. The detailed operational parameters for the laboratory-scale co-treatment of PW with sewage are summarized in Table S3.†

Analytical methods

Dissolved oxygen (DO) and pH were measured using a Hach HQ40d portable analyzer. The turbidity of wastewater was determined by using a Hach 2100AN turbidimeter. COD_{Cr} was monitored by utilizing a Lianhua 5b-3 spectrophotometer. Total organic carbon (TOC) was determined using Shimadzu TOC-VCPH analyzers. BOD_5 was detected by utilizing a WTW OxiTop IS12 analyzer. Inorganic anions and cations were measured by ion chromatography using a Dionex ICS-3000 and a Thermo Fisher Aquion ICS, respectively. Total nitrogen (TN), ammonia nitrogen (NH_4^+-N), nitrate nitrogen, nitrite nitrogen, total phosphorus (TP), total suspended solids (TSS),

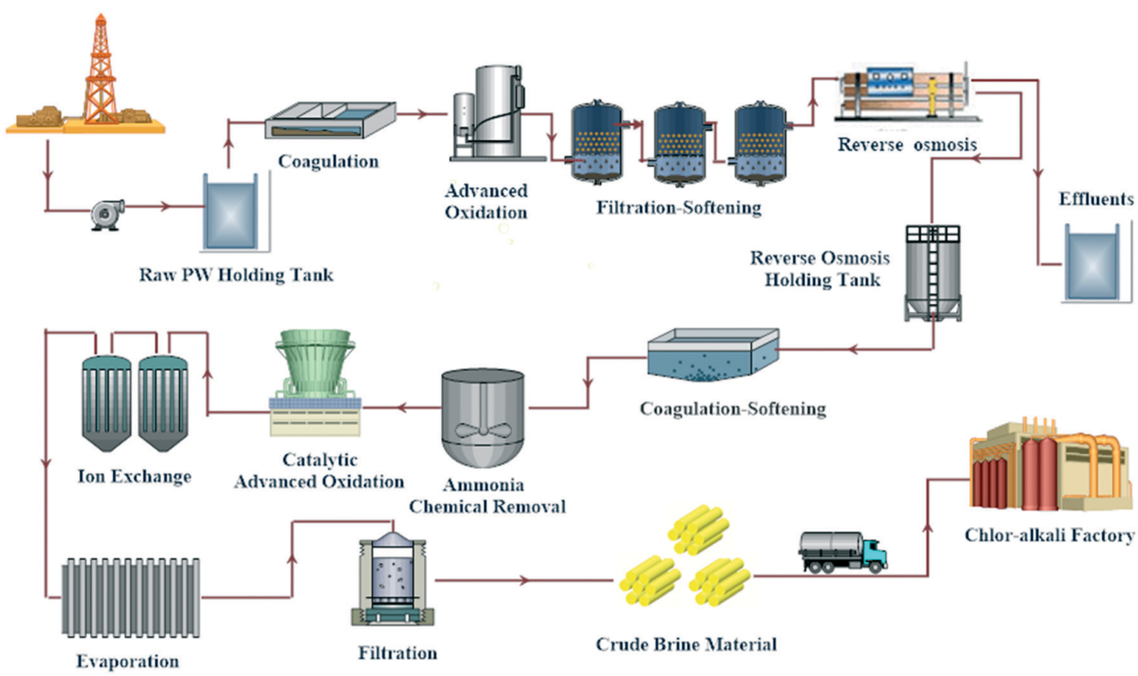

Fig. 1 Flow diagram of the laboratory-scale treatment and recycling of PW by a sequential physicochemical process.

and total dissolved solids (TDS) were determined through standard methods.[35] Volatile organic compounds (VOCs) in a typical PW sample was measured by performing thermal desorption-gas chromatography-mass spectroscopy (TD-GC-MS) using an Agilent HP-5MS capillary column (Agilent 7890A GC with 5975C MSD, Agilent Technologies, USA) with a headspace autosampler (Tekmar HT3, Teledyne Technologies, USA). Peaks were identified by using Agilent Technologies ChemStation Software in accordance with the National Institute of Standards and Technology mass spectrum library (NIST08.L).

The water acute toxicity of the PW collected from several typical shale gas wells in this field was determined by luminescent bacteria testing. Water samples were filtered with a 0.45 μm pore-diameter membrane, and the toxicity was determined using a rapid screening kit for water acute toxicity (JQ TOX-kit IV, J&Q Environmental Technologies Co., Ltd., China) in accordance with the manufacturer's recommendations and standard method.[35] The results were calculated as the luminescence inhibition rate (H, 15 min, 15 ± 1 °C) of the luminescent bacterium *Vibrio fischeri* NRRL B-11177 according to eqn (1).

$$H = [(f \cdot I_{T_0}) - I_{T_t}]/(f \cdot I_{T_0}) \times 100\% = 1 - I_{T_t}/(f \cdot I_{T_0}) \times 100\% \quad (1)$$

where I_{T_0} is the initial luminous intensity of the sample; I_{T_t} is the luminous intensity after 15 min of the sample; f is the correction coefficient, and $f = I_{C_t}/I_{C_0}$; I_{C_t} is the luminous intensity after 15 min of the control, and I_{C_0} is the initial luminous intensity of the control. The luminous intensity was measured using a Hitachi F-4600 fluorescence spectrophotometer.

Results and discussion

Characterization of shale gas PW in the shale gas field in the Eastern Sichuan Basin

Pollutant concentrations of the PW samples among the first 15 shale gas wells in the Eastern Sichuan Basin are shown in Table 1. The characteristics of the PW in the shale gas field in the Eastern Sichuan Basin varied considerably among the wells. For example, the TDS concentration exhibited an obvious fluctuation, which ranged from 4.9 g L^{-1} to 52.5 g L^{-1} (Table 1), between two close wells. The mean concentrations of TDS, COD_{Cr}, and NH_4^+-N were 26.5 g L^{-1}, 2356 mg L^{-1}, and 86.27 mg L^{-1}, respectively (Table 1). The contents of phosphates, sulfates, and heavy metals in the PW were low. For the PW centralized treated in private industrial WWTPs, the TDS present in this brine met the requirements of RO desalination (maximum TDS of 40 g L^{-1}) after effectively removing of organic compounds and particulates.[13] The content of bromide ions in this shale gas field was related to the chloride content (R^2 = 0.8281) (Fig. S2†). Bromate is typically generated from a bromide ion during an advanced oxidation process and has been studied for its high carcinogenicity and genotoxicity.[36,37] Acute toxicity tests of the raw PW samples among the wells showed that the majority of raw PW samples were at mid-toxicity levels (with an inhibition ratio between 30% and 40%) except for two samples (Fig. S3†).

In general, pollutant compositions of the PW were derived from chemical additives in the hydraulic fracturing fluid and formation brine which were produced with the nature gas after the shale gas well started production.[9–11] Potential toxic organic compounds, such as quaternary ammonium biocides and 2-butoxyethanol in the hydraulic fracturing fluid and polycyclic aromatic hydrocarbons and phthalates in the formation brine, have been regularly determined in the PW.[38] The qualitative identification of VOCs by TD-GC-MS also ascertained a group of complex organic compounds that contain C, H, O, N, S, and Cl (Tables S4†). Therefore, environmental risk assessment of the raw PW and the treatment process is important for the degradation process that is frequently accompanied by a transformation of pollutants that produce toxic products.[11,15,38]

The water quality and regional environmental regulations (*e.g.*, regulations and permits that are created by environmental protection agencies within the jurisdiction of the shale gas field to restrict the discharges from hydraulic fracturing into ambient waters) are the two deciding factors for

Table 1 Water quality of the PW in the Eastern Sichuan Basin of China

Parameters	Min.	Max.	Mean	Parameters	Min.	Max.	Mean
pH	6.45	8.29	7.00	As (mg L^{-1})	N.D.	N.D.	N.D.
TS (g L^{-1})	5.20	52.1	31.13	Ba (mg L^{-1})	5.03	558.68	170.02
TVS (g L^{-1})	0.50	26.20	14.35	Mg (mg L^{-1})	3.76	86.16	33.90
TDS (mg L^{-1})	4900	52 500	26 500	Ca (mg L^{-1})	29.52	508.69	249.50
TSS (mg L^{-1})	300	9900	2000	Fe (mg L^{-1})	5.58	150.50	87.03
COD_{Cr} (mg L^{-1})	556	3767	2356	Cd (mg L^{-1})	N.D.	N.D.	N.D.
TN (mg L^{-1})	44.27	317.40	111.59	Co (mg L^{-1})	N.D.	N.D.	N.D.
NH_4^+-N (mg L^{-1})	42.63	170.70	83.63	Cr (mg L^{-1})	0.06	2.13	0.34
TP (mg L^{-1})	0.29	14.56	3.01	Mn (mg L^{-1})	0.21	5.45	1.59
SO_4^{2-} (mg L^{-1})	N.D.	38.85	13.68	Ni (mg L^{-1})	0.03	0.71	0.17
Cl^- (g L^{-1})	2.80	24.70	13.99	Pb (mg L^{-1})	0.30	3.36	1.38
K (mg L^{-1})	30.73	746.84	240.63	V (mg L^{-1})	N.D.	0.42	0.07
F (mg L^{-1})	0.88	8.09	2.70	Zn (mg L^{-1})	0.66	7.20	3.61
Al (mg L^{-1})	N.D.	29.04	5.41	As (mg L^{-1})	N.D.	N.D.	N.D.

N.D. = Not detected

designing PW treatment processes. To date, the USA has accumulated rich experience in this aspect. Compared with the reported water quality of PW in the US shale gas fields, the PW wastewater in the Eastern Sichuan Basin has a similar pollutant composition fingerprint.[9–11] However, the TDS content in the PW in this shale gas field (26.5 g L^{-1}) is considerably lower than those in the Marcellus, Barnett–Woodford, and Bakken shale gas fields in the USA (mean TDS is above 100 g L^{-1}).[10–39] This result suggests that pressure-driven membrane processes are a cost-effective option for PW treatment compared with emerging hypersaline disposal technologies.[34]

PW treatment for discharge: laboratory and on-site pilot-scale physicochemical pre-treatment–RO process

For the suspended and colloidal substance particle removal from PW, conventional coagulation and advanced oxidation techniques were comprehensively evaluated. The order of the turbidity purification performance of raw PW was as follows: polymeric aluminum sulfate > polymeric ferric sulfate > $Al_2(SO_4)_3$ > $Fe_2(SO_4)_3$. The turbidity of raw PW was approximately 500–1000 NTU and could be lower than 1 NTU after conventional coagulation. Subsequently, six industrialized advanced and chemical oxidation techniques were assessed with a mutual comparison for the removal efficiency of COD_{Cr} (Fig. S4†). The results indicated that the combination of modified Fenton and NaClO oxidation processes achieved the highest COD_{Cr} elimination efficiency. The combination of activated potassium persulfate and NaClO oxidation processes would be another appropriate option considering the massive solid waste from the Fenton reaction (Fig. S4†). For the activated potassium persulfate oxidation, in addition to its high cost, the formation of bromate, which has high toxicity and carcinogenicity, would be another potential drawback of this process in practice.[40] Overall, the modified Fenton and NaClO oxidation processes were selected in this study as a PW pre-treatment approach after coagulation. The following multi-media filtration with artificial zeolite was operated before RO. The commercial artificial zeolite has an inefficient ammonia removal rate of 24.6% (Fig. 2) on account of the 3.5% salinity of the PW. For an efficient ammonia elimination and alleviation of the membrane fouling of RO, NaOH-modified artificial zeolite was utilized. It remarkably enhanced the ammonia removal rate by 60% under the same conditions (Fig. S5 and S6†). The content of contaminants in the effluents was below the vast majority of the current pollutant discharge or emission standards of industrial wastewater in China (Fig. 2 and Table S5†). Furthermore, membrane fouling was controlled in a reasonable range as a result of the systematic physicochemical pre-treatments.

A 5 m^3 d^{-1} pilot-scale PW treatment station was constructed and implemented near a typical well in the shale gas field in the Eastern Sichuan Basin. The PW disposal approach was based on the laboratory-scale sequential physicochemical treatment route. The pilot-scale apparatus was operated formally after the initial adjustment period. The 15 days successive operational result is shown in Fig. 4. Organic carbon and inorganic nitrogen compounds were efficiently removed. This outcome coincided with the laboratory-scale experimental results. The concentrations of COD_{Cr}, NH_4^+-N, and TN in the permeate water from RO were far below the

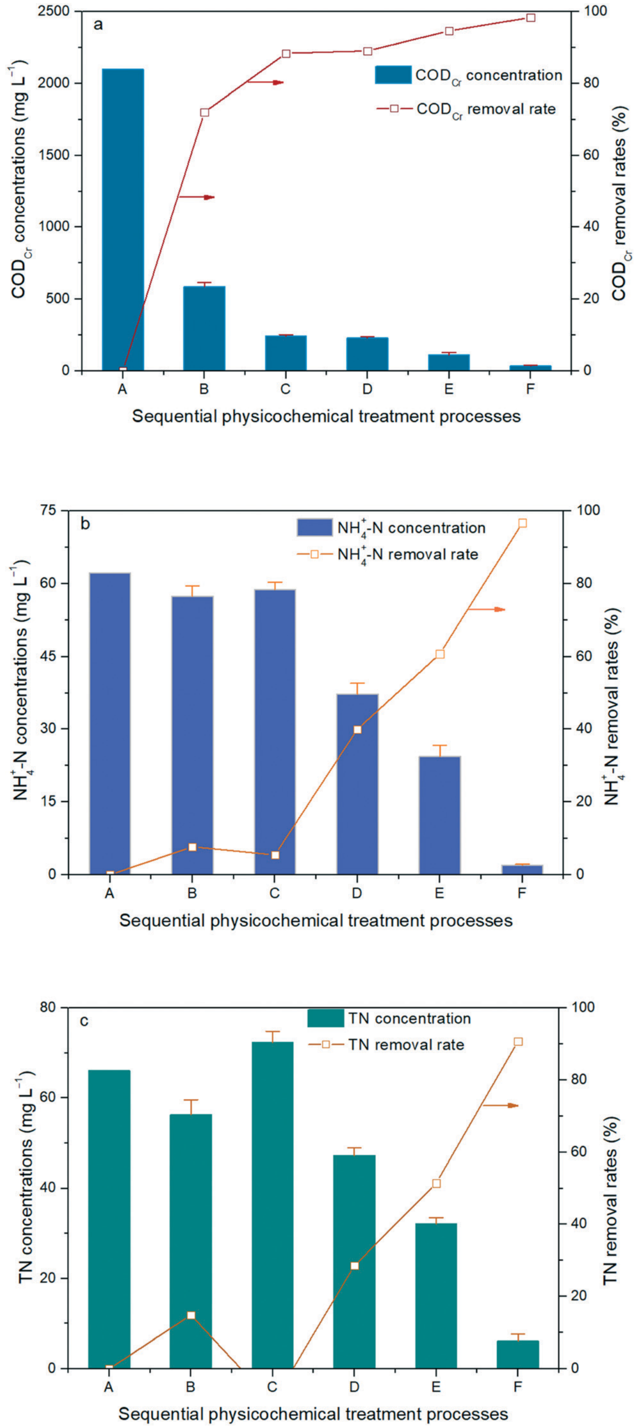

Fig. 2 Removal profiles of (a) COD_{Cr}, (b) NH_4^+-N, and (c) TN from PW during the laboratory-scale sequential physicochemical treatment (A. raw PW; B. coagulation-modified Fenton process; C. NaClO oxidation; D. zeolite adsorption; E. activated carbon filtration; F. RO).

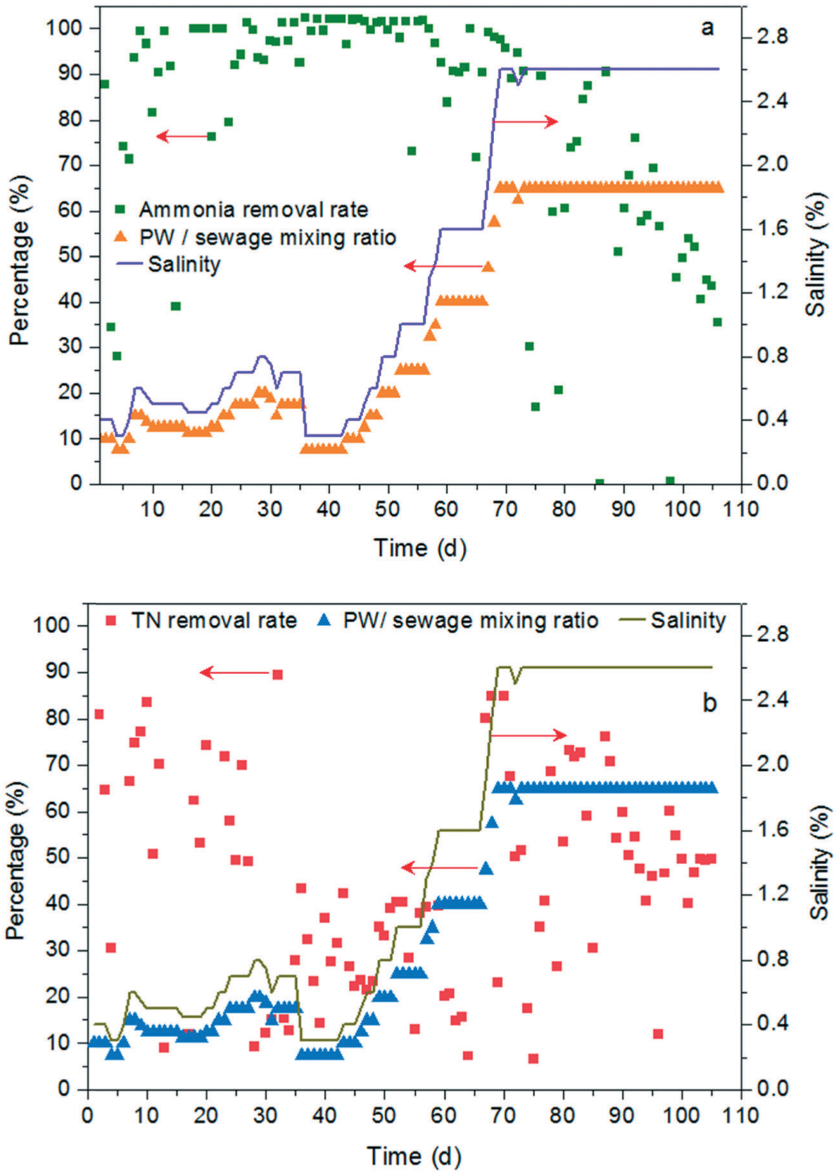

Fig. 3 Profiles of ammonia and TN removal by laboratory-scale co-treatment of pre-treated PW and domestic wastewater.

limitation level of the emission standard of pollutants for the petroleum chemistry industry in China.

The results from the laboratory- and pilot-scale pre-treatment–RO process show that organic compound mineralization and salt desalination of PW in this field were technically feasible. Currently, RO is the most applied cost-effective technology to treat PW with low and moderate salinity for direct discharge or reuse.[13] Recently, a combined ultrafiltration (UF) – RO process was successfully applied for the treatment of PW with a relatively low TDS content (18.9 g L^{-1}) in the Weiyuan shale gas field, which is located in the southwestern Sichuan Basin of China.[27] Although improved operational performance can be achieved by applying advanced UF and RO membranes,[41] effective pre-treatment approaches are apparently the major factors that reduce membrane fouling.[42] However, beyond the well-established and tested RO desalination technology, the effectiveness of the pre-treatments to alleviate the reversible and irreversible fouling during real PW desalination still needs to be tested. In general, mineral, particulate, colloidal, and organic fouling result in internal fouling, cake layer formation, and pore blocking of the RO membrane.[42] Physical and chemical pre-treatments in oil and conventional natural gas industries are usually applied as reference in the PW pre-treatment, such as coagulation and electrocoagulation.[18,42] In the present study, Fenton and sodium hypochlorite oxidation showed effective organic compound removal performance through laboratory- and pilot-scale tests (Fig. 4 and S4†). For the chemical degradation of refractory components (*e.g.*, landfill leachate), combining Fe^{2+} and NaClO has a higher COD removal rate of landfill leachate than individual Fe^{2+} coagulation or NaClO oxidation.[43] Redundant Fe^{2+} during the second dosing of ferrous

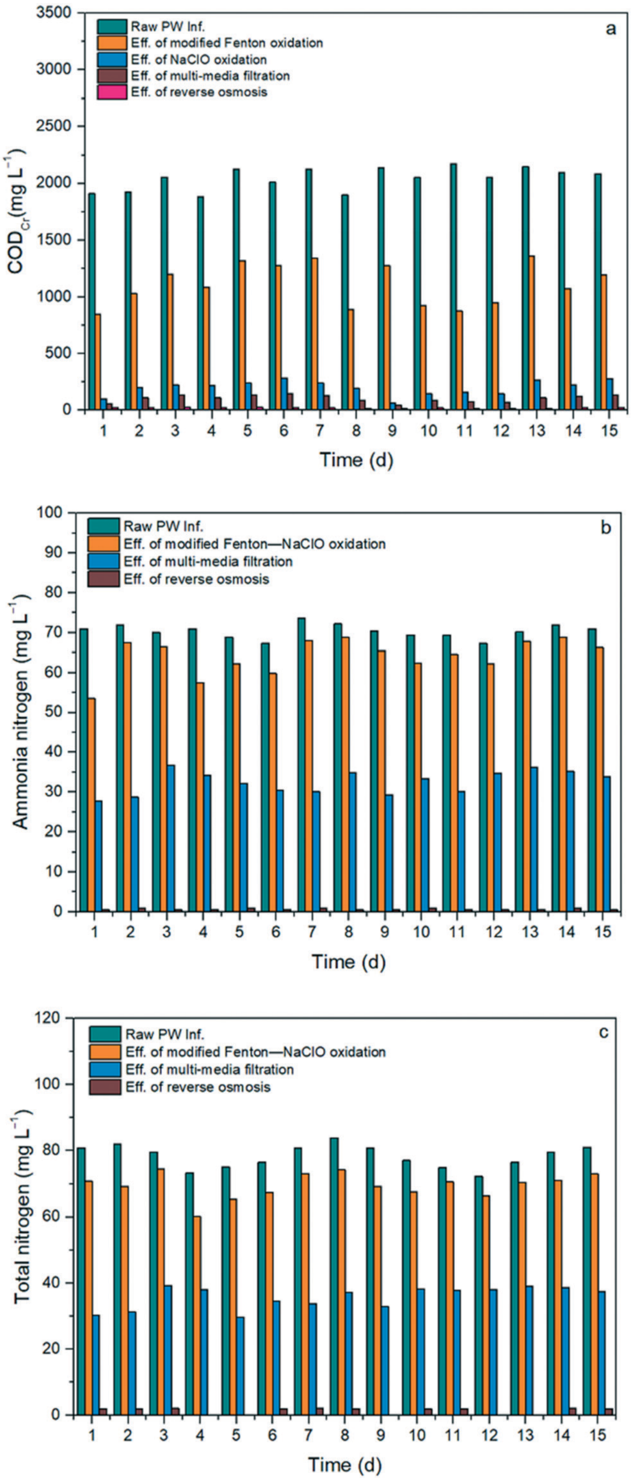

Fig. 4 Removal profiles of (a) COD_{Cr}, (b) NH_4^+-N, and (c) TN from PW using a pilot scale of the sequential physicochemical treatment in the shale gas field in the Eastern Sichuan Basin.

salts in the Fenton process might improve the COD removal performance at the NaClO oxidation stage in this experiment. One drawback of the Fenton–NaClO process for PW treatment is producing considerable ferric hydroxide excess sludge (3.83 g L^{-1}). A new electrochemical Fenton-type concept, where HOCl is generated from chloride ions and substitutes for H_2O_2 in the conventional Fenton reaction, has been developed in recent years and is being studied for its applicability to dispose wastewater that contains concentrated chloride ions.[44,45] The new Fe^{2+}/HOCl electrochemical Fenton-type process could effectively promote the reusability of Fe^{3+} that contains sludge and could lighten the burden of solid waste disposal during the pre-treatment process.

Overall, compared with the reported RO pre-treatments for PW disposal, the present study established a more effective process for elimination of colloids, mineral elements, and organic compounds.

PW RO concentrate treatment for external reuse: laboratory scale of sequential physicochemical processes

The planning-centralized PW treatment plant in the shale gas field in the Eastern Sichuan Basin is in close proximity to a large chlor-alkali enterprise, which requires a large number of brine as raw material to produce sodium hydroxide. The RO concentrates, which have nearly a half volume of raw PW, were advanced treated and evaporative concentrated to a salinity of above 23% and the pollutant concentrations below the brine quality standard limit were reached (Table S2†). Colloids and calcium, and magnesium ions were effectively removed through coagulation and softening treatment processes. The vast majority of ammonia (94.8%) was removed by NaClO oxidation, and the residual ammonia was below 4.0 mg L^{-1}. The following advanced oxidation for degrading refractory organic compounds was the main challenge in recycling the PW RO concentrate. Batch tests of O_3–H_2O_2 oxidation and dimensionally stable anode (DSA)-type electrochemical oxidation were performed comparatively (Table S2†). The results indicated that the O_3–H_2O_2 process exhibited effective TOC removal rates. The residual TOC in the concentrate was below 1.6 mg L^{-1}. The TOC removal rate was unstable in the DSA-type electrochemical oxidation, although the experimental parameters were comprehensively adjusted. Overall, the quality of the concentrated brine satisfied the requirements of the chlor-alkali enterprise after bromine and iodine ion exchange and evaporation.

The internal reuse of PW for subsequent hydraulic fracturing is a conventional practice during the development of well drilling after preliminary treatments.[17] Compared with the surface discharge standards, the water quality of this internal reuse is relatively conservative and has usually no strict limitation on TDS.[17] The present study focused on the external reuse of wastewater from shale gas fields when drilling and hydraulic fracturing are finished. Until recently, the use of RO concentrate from PW desalination processes has been rarely reported. Given these factors, final reuse patterns and advanced treatment technologies are necessary to optimize design and management. In general, the sustainable treatment, management, and recycling resources from RO rejects have become major challenges worldwide.[46] Thermal and membrane-based technologies are the existing and currently applied processes, although FO and MD coupled with crystallization have received considerable attention as cost-effective emerging technologies for RO reject disposal.[24,47] In the present study, the RO rejects from the PW treatment line were recovered as raw brine for the chlor-alkali industrial requirement. This technique is less energy intensive than evaporative crystallization. The key point of the RO rejection for this recycling process was to eliminate ammonia and TOC from the concentrate. The water quality of the raw brine reception standard is more stringent than the one reused for subsequent hydraulic fracturing. According to the process requirements of chlor-alkali industrial companies, the parameters that need to be limited include the following: TOC < 7 mg L^{-1}, ammonia < 2 mg L^{-1}, iodine < 1 mg L^{-1}, iron < 2 mg L^{-1}, strontium < 0.1 mg L^{-1}, silicon < 0.1 mg L^{-1}, and bromine < 28 mg L^{-1}. Therefore, advanced catalytic oxidation of refractory organic matters and interception of inorganic and metal elements in the PW RO concentrate are indispensable approaches. In this study, O_3/H_2O_2 oxidation achieved a mineralization of refractory organic matters in the RO concentrate, thereby indicating the potential application of this combined technique for advanced treatment of high salinity wastewater. Similar reports have confirmed that the O_3/H_2O_2 process is a promising technology for treating organic compounds in typical wastewater matrices, such as landfill leachate and disinfected by-products.[48,49] Besides being reused as raw brine in chlor-alkali industries, other potential options for the cycling of RO concentrates include recovery as industrial-grade sodium chloride for snow melting, textile printing, well drilling, and raw salt for sodium carbonate production. However, the corresponding industrial standards are inadequate to date.

PW biological co-treatment with sewage in WWTPs: laboratory scale of the sequential chemical pre-treatment–biological process

A laboratory-scale co-treatment of PW with domestic wastewater testing was performed to evaluate the feasibility of the biological treatment of PW. In an initial trial, PW without pre-treatment was mixed with sewage and tested. The results indicated that raw PW had a significant inhibition effect on biological process performance, although the PW-to-sewage ratio was maintained below 15% (data not shown). As such, PW was pre-treated by modified Fenton and NaClO oxidation processes which were conducted before co-treatment with sewage. Fig. 3 illustrates the ammonia and TN removal from the mixed wastewater when the post-treated PW-to-sewage ratio increased from 10% to 65%. The co-treatment process was operated for 108 days. The NH_4^+-N removal efficiency of the mixed wastewater after two weeks of adaptation reached approximately 85% when the ratio was maintained below 50% (Fig. 3a). However, the denitrification performance showed an opposite result (below 20%)(Fig. 3b). The mixed ratio of the two wastewaters was increased to 65% after 68 days of operation when the salinity reached 26 g L^{-1}; moreover, the nitrification efficiency was obviously affected (Fig. 3a). However, an unexpected increment in denitrification efficiency was achieved when the mixed ratio was maintained at as high as 65% (Fig. 3b).

PW co-treatment with sewage in municipal WWTPs has been a cost-effective PW management strategy in shale gas fields in the USA.[14] However, the negative effects of high TDS and refractory organic compounds in the PW on conventional biological sewage disposal processes have limited the long-term implementation of this strategy.[14] Moreover, information on modified or advanced co-treatment technologies to improve the operational stability of biological treatment of PW, such as necessary pre-treatment processes and biological reactor configurations, is still lacking.[17,50] Riley and co-workers indicated that seeding functional bacteria present in the raw PW could improve the removal rates of organic compounds in a biologically active filtration reactor treating PW.[50] The present study provides a new modification process of the co-treatment of PW with municipal sewage by chemical pre-treatment of PW before mixing with sewage. The following biological process realized a complete ammonia removal at a mixed ratio of pre-treated PW of 65%. The results revealed that PW with an appropriate pre-treatment can be successfully imported into the WWTPs with a limited mixed ratio of 5–15% to realize a cost-effective PW disposal. Although the importance of biological co-treatment of PW was demonstrated in the present laboratory-scale study, the sequential chemical–biological process to treat this industrial wastewater is usually case-specific due to the uncertainty of the influent and the complexity of microbial ecology.[51] Further studies must focus on improving PW pre-treatment methods to reduce the toxicity and enhance the biodegradability of PW.

Economic evaluation of PW desalination and RO concentrate recycling processed in a full-scale centralized shale gas PW treatment plant

The operating cost of a centralized full-scale shale gas PW treatment plant with a 1500 m^3 d^{-1} capacity is presented in Table 2. The results were calculated on the basis of the PW desalination, RO concentrate advanced treatment, and recycling processes. The total treatment and recycling cost of 1 m^3 of PW from the shale gas field in the Eastern Sichuan Basin was $12.114 per m^3. As expected, the most significant cost of the entire treatment route included the advanced oxidation of raw PW and membrane concentrate, brine evaporation, and sludge disposal (Table 2). The operation cost of the PW desalination was high, although the PW of this shale gas field had similar salinity to that of seawater. Previous model studies have revealed that the least work required to desalinate PW is nearly nine times more than desalinating seawater at 50% recovery.[34] High additional cost is required to remove hydrophobic organics and colloidal particles in PW to achieve low membrane fouling during ultrafiltration and RO

Table 2 Operating costs of a centralized shale gas PW treatment plant considered on the basis of advanced oxidation, desalination, and membrane concentrate recycling processes (\$ per m^3)

Stages	PW desalination				RO concentrate advanced treatment and recycling				
Cost[a] (\$ per m^3)	Coagulation	Fenton–NaClO oxidation	Multi-media filtration	Ultrafiltration-RO	Pre-treatment	O_3-H_2O_2 oxidation	Ion exchange-carbon filtration	Evaporation	Brine recycling
Electricity	0.005	0.034	0.028	1.110	0.011	0.612	0.022	5.980	0.015
Chemicals	0.039	0.854	0.050	0.030	0.092	0.145	0.095	0.050	—
Sludge	0.625	1.250	—	—	0.773	—	—	—	—
Labor	0.034	0.034	0.034	0.034	0.034	0.034	0.034	0.034	0.034
Total	0.700	2.169	0.109	1.171	0.910	0.791	0.151	6.064	0.049
	4.149				7.965				

[a] Costs are reported in US dollar for treating 1 m^3 of raw PW from the shale gas field in the Eastern Sichuan Basin, and the capacity of the centralized shale gas PW treatment plant is 1500 m^3 d^{-1}. The selling price of the purified brine from the membrane concentrate is excluded.

desalination.[34] Further studies should optimize the pre-treatment efficiency and reduce sludge production provided that membrane fouling is restricted at a low level. The maximum operational cost in the membrane concentrate recycling process is the energy consumption of the MVC (Table 2). A similar study has indicated that the energy consumption for single- and dual-effect MVC systems that treat PW at medium and large scales are 23–42 and 20 kW h m^{-3}, respectively.[34] Overall, the RO system showed a cost efficiency advantage over other desalination techniques when treating PW with a moderate recovery on the basis of the salinity of PW from the shale gas field in the Eastern Sichuan Basin. The optimization of the operation efficiency of evaporative systems for brine recycling can significantly reduce the total expense ratio.[34]

Comparison of the combined treatment process with the reported or existing ones in centralized shale gas PW treatment plants

The research on the shale gas industry has been rapidly developing since 2008, and the strategy of PW management has gradually shifted from primary disposal to profound treatment and resource recovery due to the increasing environmental criteria.[17,52] However, the feasibility of the integral technology roadmap of PW treatments for high-grade discharge in certain private centralized shale gas PW treatment plants has yet to be explored in detail.[13,17,18] Only several integral treatment processes for PW from conventional oil & gas industries have been proposed.[29,31] An applicable treatment process is not merely a simple combination of processing units but is also an optimized result in consideration of technical, environmental, and economic factors.[13]

In comparison with the reported centralized treatment processes of conventional oil & gas PW with similar TDS levels (<40 g L^{-1}), a consensus had been reached on the physicochemical methods and RO processes for TDS removal. The reported pilot process consisted of warm softening, coconut shell filtration, cooling, trickling filtration, ion exchange and reverse osmosis to remove hardness, silica, boron, TOC and ammonia.[29,31] This study also established a broadly similar technology roadmap, including pre-treatment units, secondary pre-treatment units before membrane separation, pressure-driven membrane separation, and the membrane concentrate treatment or reuse.

Nevertheless, the present study still indicates that the biological unit is unsuitable for shale gas PW treatment, and increased profound physicochemical pre-treatments are needed to reduce the TOC before RO desalination. For RO concentrate reuse, a conventional disposal by deep well injection has been investigated in the literature.[31] Meanwhile, this study proposes a new reuse method, that is, the recycling of shale gas PW RO concentrate as a raw brine material in chlor-alkali enterprises.

Conclusion

This study assessed the feasibility of an integral treatment process of sequential pre-treatment and pressure-driven membrane desalination, which was proposed for the first private centralized shale gas PW treatment plant in the Eastern Sichuan Basin, China. The reuse of the membrane concentrate and co-treatment of PW with sewage by biological processes were also evaluated. The results included technical principles and policy implications, discussed as follows.

(1) For the PW treatment of discharge, a sequential pre-treatment and pressure-driven membrane desalination process including Fenton–NaClO oxidation, multi-media filtration, and RO processes was demonstrated where bulk pollutants in PW were eliminated. The content of contaminants in the RO effluents was below the vast majority of the current pollutant discharge standards of oil & gas industrial wastewater in China.

(2) For the external reuse of the corresponding PW RO concentrate, a novel recycling route was proposed to rationally dispose the RO concentrate. The RO concentrate was recycled as a raw brine material for a chlor-alkali enterprise through a physicochemical advanced treatment process.

(3) For the PW co-treatment with sewage by biological process, salinity fluctuation, chemical pre-treatment toxicity, and resistance and resilience of bioreactors after fluctuations may heavily influence the planning, design, and construction of PW treatment plants, although the coupled chemical–

biological process for treating PW is a potential cost-effective treatment technique.

(4) Our results indicate that the current regulations, such as the Technical Specification for Oil Production Wastewater Treatment (HJ2041-2014), and the Technical Specification for Wastewater Treatment in Petroleum Refining Industry (HJ2045-2014), are unsuitable for shale gas PW treatment. New technical specifications for the treatment of specific industrial wastewater, that is, gas- and oil-field PW in China, must be developed. The toxicity and NORM content should be included in the standard. Moreover, new standards for industrial salt or brine, which is recycled from RO concentrate solutions of shale gas PW, should be developed and adopted.

Conflicts of interest

There are no conflicts to declare.

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