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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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Supporting data: 12 pages, 5 tables, 6 figures.

Table S1 Operational strategy and parameters for the laboratory-scale PW treatment

Step	Treatment process		Parameters
1	Pretreatment and combined advanced chemical oxidation	Coagulation	Dosing $Al_2(SO_4)_3$ with pH = 6.0
2		Modified Fenton oxidation[a]	H_2O_2 = 10 mL/L; $FeSO_4 \cdot 7H_2O$ = 0.5 and 2.5 g/L; pH = 3.2
3		NaClO oxidation	NaClO = 1 mL/L; pH = 7.0
4		Residual chlorine removal	Na_2SO_3 dosing
5	Multi-media filtration	Sand-artificial zeolite filtration	-
6		Activated carbon filtration	-
7	Desalination	RO	RO membrane material:GE1812; Pressure = 3.0–4.0 MPa; Pure water conductivity = 450–650 μS/cm

a. Modified Fenton oxidation was designed by dosing $FeSO_4 \cdot 7H_2O$ twice in an entire Fenton oxidation experiment.

Table S2 Operational strategy and parameters for recycling RO concentrate

Step	Treatment process		Parameters
1	Pretreatment	Coagulation-softening	-
2		NaClO oxidation	NaClO = 21 mL/L; pH = 10.0–11.0
3	Advanced oxidation[a]	O_3-H_2O_2 oxidation	O_3 gas flow rate = 30 L/h; pH = 11.0
4		Electrochemical oxidation	DSA-type anode; Stainless steel cathode; Current = 0.77 A; pH = 7.5
5	Advanced filtration	Ion exchange	D-301anion exchange resin; Filtration flow rate = 1.0 L/h
6		Activated carbon filtration	Granular activated carbon; Filtration flow rate = 1.0 L/h
7	Concentration	Evaporation concentration	-

a. Removal efficiencies of residual refractory organic matters in the pretreated RO concentrate by O_3-H_2O_2 oxidation and DSA-type electrochemical oxidation techniques were compared.

Table S3 Operational strategy and parameters of MBBR system for the co-treatment of PW with domestic wastewater

Reactor volume (L)	Sequencing batch operational mode	HRT (h)	DO in Oxic stage (mg/L)	MLSS concentration	Biofilm carriers
8.0	Feeding (0.25 h)/Anoxic (2 h)/Oxic (2 h)/Anoxic (2 h)/Oxic (1 h)/Setting (0.5 h)/Withdrawing (0.25 h)	8.0	4.5–6.5	3000–4000 mg/L	AnoxKaldnes K5 type; Fill ratio = 30%

Table S4 Representative of identified molecules in the PW from the Eastern Sichuan Basin by TD-GC-MS analysis

Formula	Compound name	CAS
$C_7H_5N_5O_3$	Pterin-6-carboxylic acid	948-60-7
$C_9H_{11}F_2NO_3$	Benzeneethanamine	152434-78-1
$C_2H_6N_2O_2$	Hydroxyacetic acid	3530-14-1
$C_{10}H_{18}O_2$	8-Methyl-6-nonenoic acid	21382-25-2
$C_{21}H_{34}S_2$	cyclic ethylene mercaptole	2759-86-6
$C_{14}H_{25}F_3O_2$	2-Trifluoroacetoxydodecane	1894-68-4
$C_8H_{24}O_4Si_4$	Cyclotetrasiloxane	556-67-2
$C_{22}H_{45}Cl_3Si$	Docosyltrichlorosilane	7325-84-0
$C_{13}H_{28}$	5-ethyl-5-methyldecane	17312-74-2
$C_{31}H_{56}$	Pentacosan-13-ylbenzene	6006-90-2
$C_{11}H_{21}ClO$	4-Chloro-3-n-hexyltetrahydropyran	66555-66-6
$C_{12}H_{24}O$	Z-2-Dodecenol	69064-36-4
$C_{10}H_9NO_2$	4-Methoxy-2(1H)-quinolone	27667-34-1
$C_{17}H_{36}$	2,6,10-trimethyltetradecane	14905-56-7
$C_9H_{16}BrNO$	2-Piperidinone	195194-80-0
$C_{20}H_{34}O$	8,11,14-Eicosatrienoic acid	1783-84-2
$C_{37}H_{76}O$	1-Heptatriacotanol	105794-58-9
$C_{16}H26O_3$	2-Dodecen-1-yl(-)succinic anhydride	19780-11-1
$C_{16}H_{30}O$	11-Hexadecyn-1-ol	65686-49-9
$C_{14}H_{24}O_2$	3-Tetradecanynoic acid	55182-76-8
$C_{40}H_{56}$	πCarotene	7235-40-7
$C_{15}H_{28}O$	2-Pentadecyn-1-ol	2834-00-6
$C_{15}H_{28}O$	Z,Z-2,5-Pentadecadien-1-ol	139185-79-8
$C_{15}H_{24}O$	Butylated Hydroxytoluene	128-37-0
$C_{22}H_{38}O_2$	Cyclopropaneoctanoic acid	10152-71-3
$C_{12}H_{20}O_4$	trans-Traumatic acid	6402-36-4
$C_{15}H_{26}O_2$	Geranyl isovalerate	109-20-6
$C_{16}H_{34}N_2O$	16-Hexadecanoyl hydrazide	2619-88-7
$C_{16}H_{22}O_2$	1,1'-Butadiynylenedicyclohexanol	5768-10-5
$C_{19}H_{32}O_2$	9-Octadecen-12-ynoic acid, methyl ester	56847-05-3
$C_{18}H_{38}N_2O$	Stearic acid hydrazide	4130-54-5
$C_{16}H_{30}O$	7-Hexadecenal, (Z)-	56797-40-1
$C_{10}H_{16}O_2$	2-Decanynoic acid	1851-90-7
$C_{14}H_{24}O_2$	2-Myristynoic acid	67587-19-3

Table S5 Representative wastewater discharge standards of oil & gas industry in China

Items ($mg \cdot L^{-1}$, except for dimensionless pH)	Emission standard of pollutants for petroleum chemistry industry (GB31571-2015)		Emission standard of pollutants for petroleum refining industry (GB31571-2015)	
	Direct discharge [a]	Indirect discharge [b]	Direct discharge	Indirect discharge
pH	6.0-9.0	-	6-9	-
TSS	70	-	70	-
COD_{cr}	60 100 [c]	-	60	-
BOD_5	20	-	20	-
NH_3-H	8.0	-	8.0	-
TN	40	-	40	-
TP	1.0	-	1.0	-
TOC	20 30 [c]	-	20	-
Petroleum-like	5.0	20	5.0	20
Sulfide	1.0	1.0	1.0	1.0
Fluoride	10	20	-	
Volatile phenol	0.5	0.5	0.3	0.5
Cu	0.5	0.5	-	-
Total cyanide	0.5	0.5	0.3	0.5

a. Direct discharge : wastewater discharged to municipal WWTPs or sewage pipe network.

b. Indirect discharge : wastewater discharged to private industrial WWTPs.

c. Wastewater from acrylonitrile- acrylic fibres, caprolactam, epichlorohydrin, 2,6-di-tert-butyl-4-methylphenol, pure terephthalic acid, cresol, epoxide propane, and naphthalene production factories.

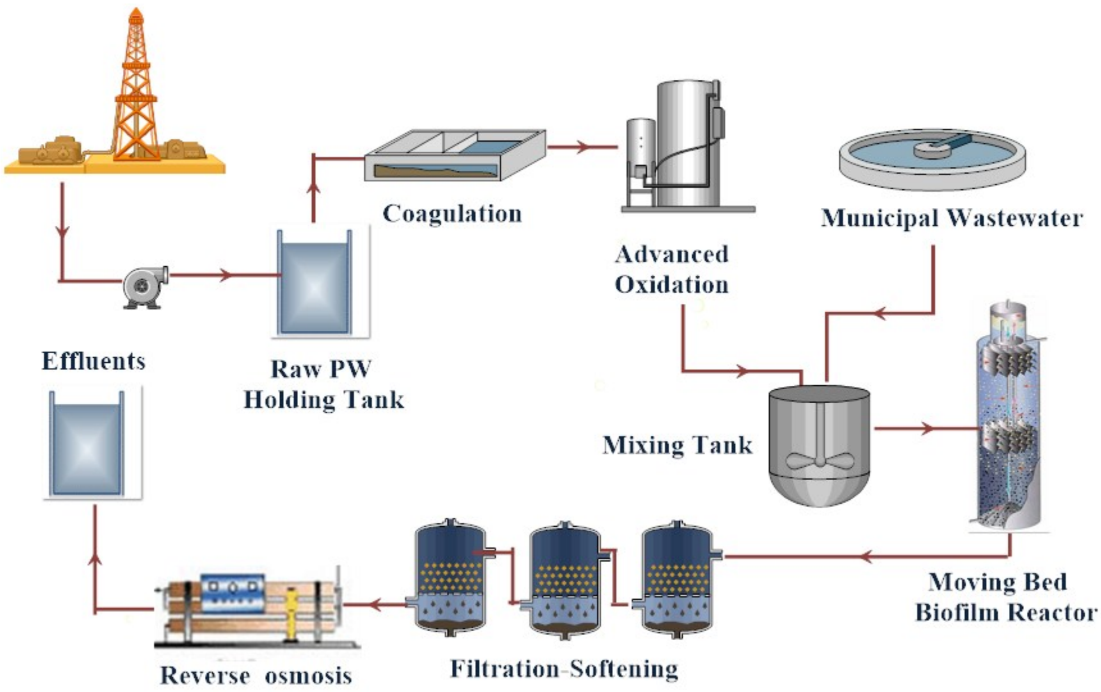

Fig. S1 Flow diagram of the laboratory-scale co-treatment of PW and domestic wastewater.

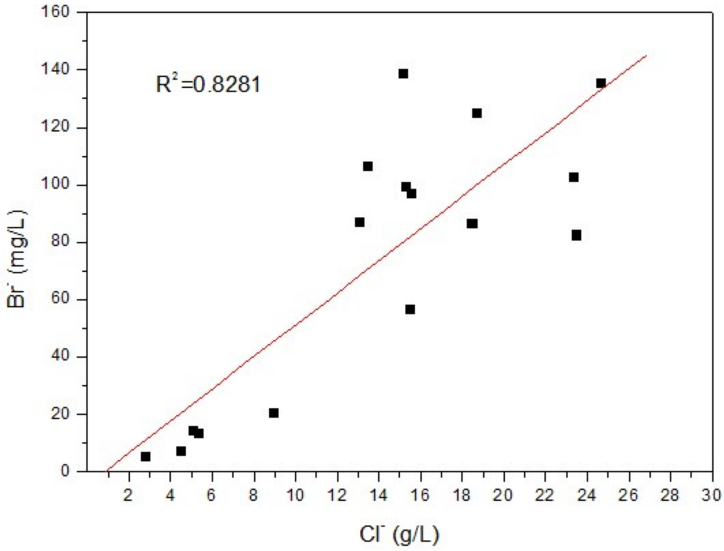

Fig. S2 Relationship of Cl^- and Br^- among PW wells in the shale gas field in the Eastern Sichuan Basin.

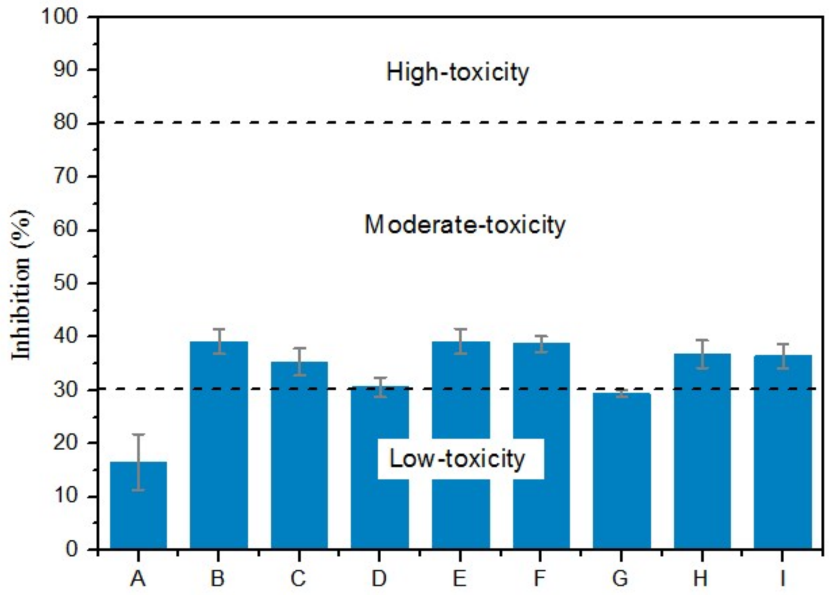

Fig. S3 Acute toxicity tests of the raw PW samples among nine wells represented as the luminescence inhibition rate (low-toxicity level: inhibition ratio <30%; mid-toxicity level: ≤30% inhibition ratio ≤80%; high-toxicity level: inhibition ratio >80%).

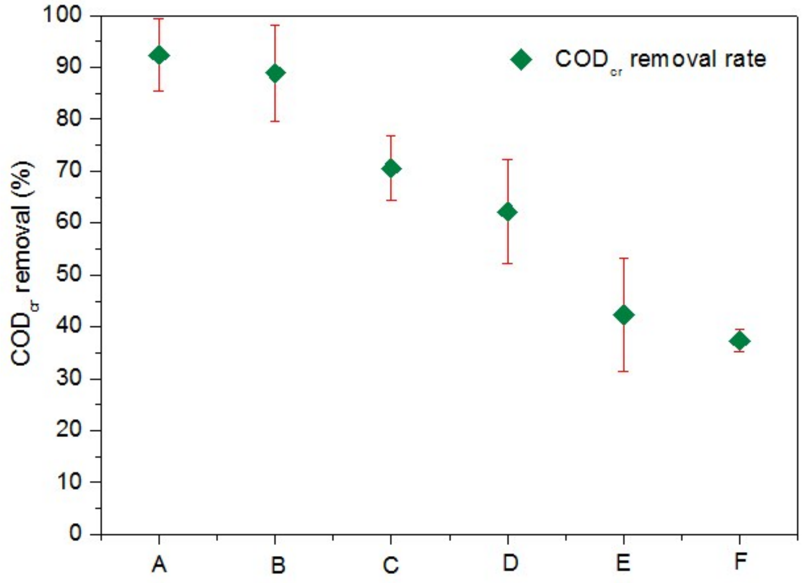

Fig. S4 Comparison among different advanced and chemical oxidation processes on the removal of COD_{cr} (A. Modified Fenton–NaClO oxidation; B. Activated potassium persulfate– NaClO oxidation; C. NaClO oxidation; D. Modified Fenton; E. Activated potassium persulfate; F. Fenton).

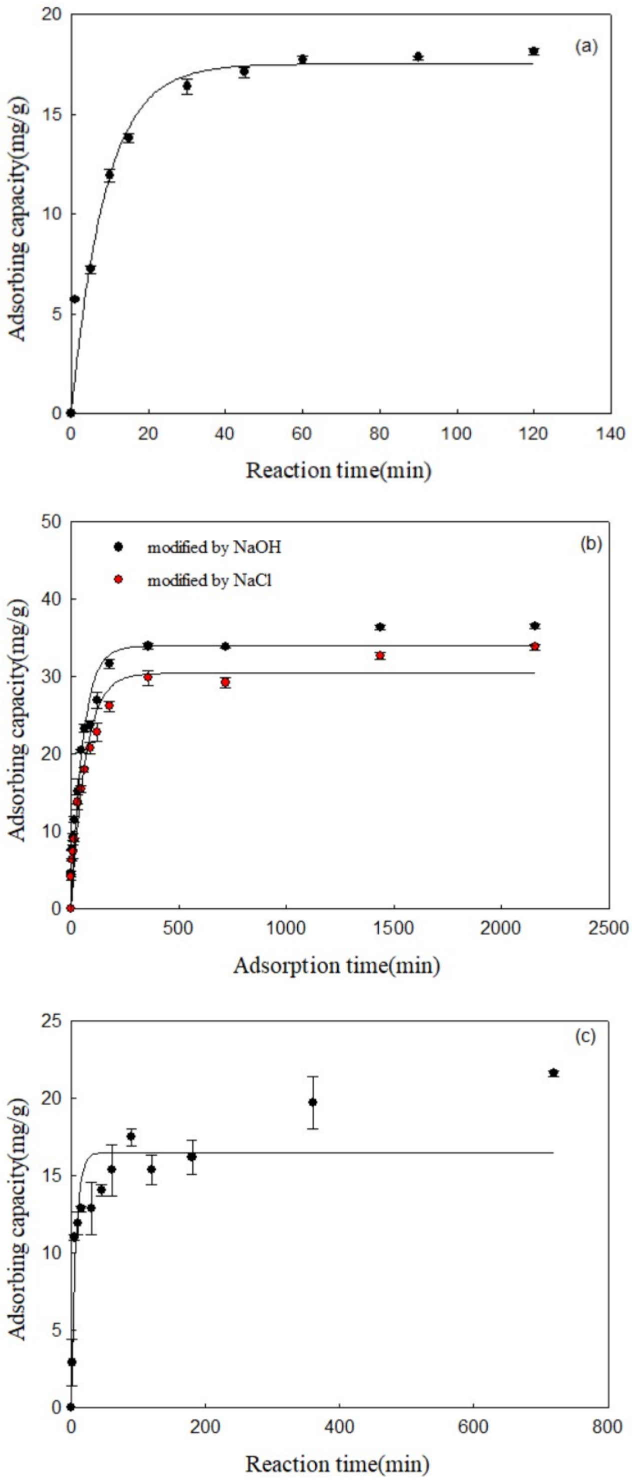

Fig. S5 First-order kinetic fitting curve of a modified artificial zeolite for ammonia adsorption in deionized water (a. Raw artificial zeolite; b. NaOH- and NaCl-modified artificial zeolite; c. HCl-modified artificial zeolite).

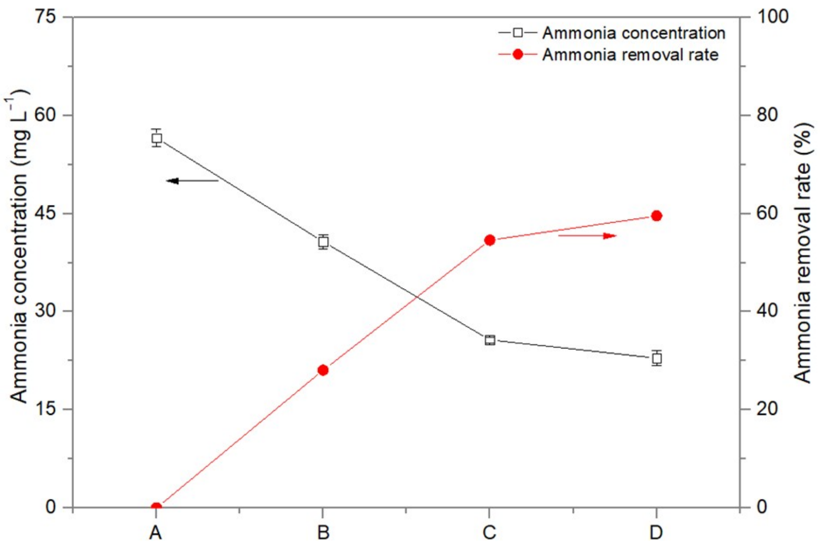

Fig. S6 Ammonia removal rate of pretreated PW by a modified artificial zeolite (A: Sequential advanced oxidation pretreated PW; B. Filtration with a raw artificial zeolite; C. Filtration with a NaCl-modified artificial zeolite; D. Filtration with a NaOH-modified artificial zeolite).