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Environmental Chemistry

Supplementary Material

Coal chemical industry membrane concentrates: characterisation and treatment by ozonation and catalytic ozonation processes

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S1 Additional experimental details and results

Table S1. Summary of wastewater analysis methods used in this study.

Parameters	Unit	Methods
Ca	mg/L	Atomic absorption spectrophotometry (GB/T 11905-1989)^
Mg	mg/L	
Fe	mg/L	Flame Atomic absorption spectrophotometry (GB/T11911-1989)
Mn	μg/L	
K	mg/L	Flame Atomic absorption spectrophotometry (GB/T11904-1989)
Na	mg/L	
Al	μg/L	Inductively coupled plasma mass spectrometry (HJ 700-2014)
Cl^{-}	mg/L	Ion chromatography (HJ 84-2016)
F^{-}	mg/L	
Total dissolved P	mg/L	
SO_4^{2-}	mg/L	
NO_3^{-}	mg/L	
Sulfide	mg/L	Methylene blue spectrophotometry
Colloidal Si	mg/L	Silicomolybdic blue colorimetry
Turbidity	NTU	Turbidity meter
NH_4-N	mg/L	Nesster's reagent colorimetry (HJ 535-2009)
TP	mg/L	Ammonium molybdate spectrophotometry
TSS	g/L	Weight
BOD_5	mg/L	BOD_5 standard method
CO_3^{2-}	mM	Titration
HCO_3^{-}	mM	
Alkalinity ($CaCO_3$)	mg/L	
pH		pH meter
Conductivity	μs/cm	Conductivity meter
Hardness ($CaCO_3$)	mg/L	EDTA titration
COD	mg/L	COD_{Cr} reagent (GB 11914-89)^^
TOC speciation	mg/L	LC-OCD for high salinity mode

^ Wet digestion method.

^^ COD correction in the presence of high Cl^{-} concentrations: Develop a calibration curve for COD value, COD_{Cl}, as a function of Cl^{-} concentration by measuring COD of pure NaCl solution (NaCl dissolved in MQ water). The COD value of the wastewater samples were obtained by subtracting the

COD_{Cl} value of the corresponding Cl^- concentration determined through IC testing from the measured COD value of the samples.

Table S2. Charge balance analysis of the measurement results.

C1#			C2#			C13#			M1#			CW1#		
[Cat] M	[An] M	*D* %	[Cat] M	[An] M	*D* %	[Cat] M	[An] M	*D* %	[Cat] M	[An] M	*D* %	[Cat] M	[An] M	*D* %
0.20	0.22	5.32	0.19	0.23	9.26	0.28	0.35	11.2	0.57	0.71	11.1	0.11	0.16	19.5

[Cat], [An] and *D* stand for the sum of cations, the sum of anions and charge difference respectively.

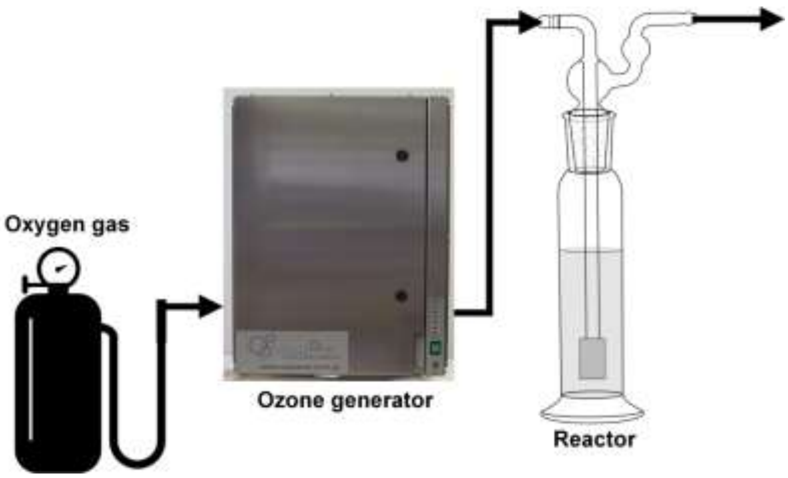

Figure S1. Schematic representation of the pure ozonation and catalytic ozonation system.

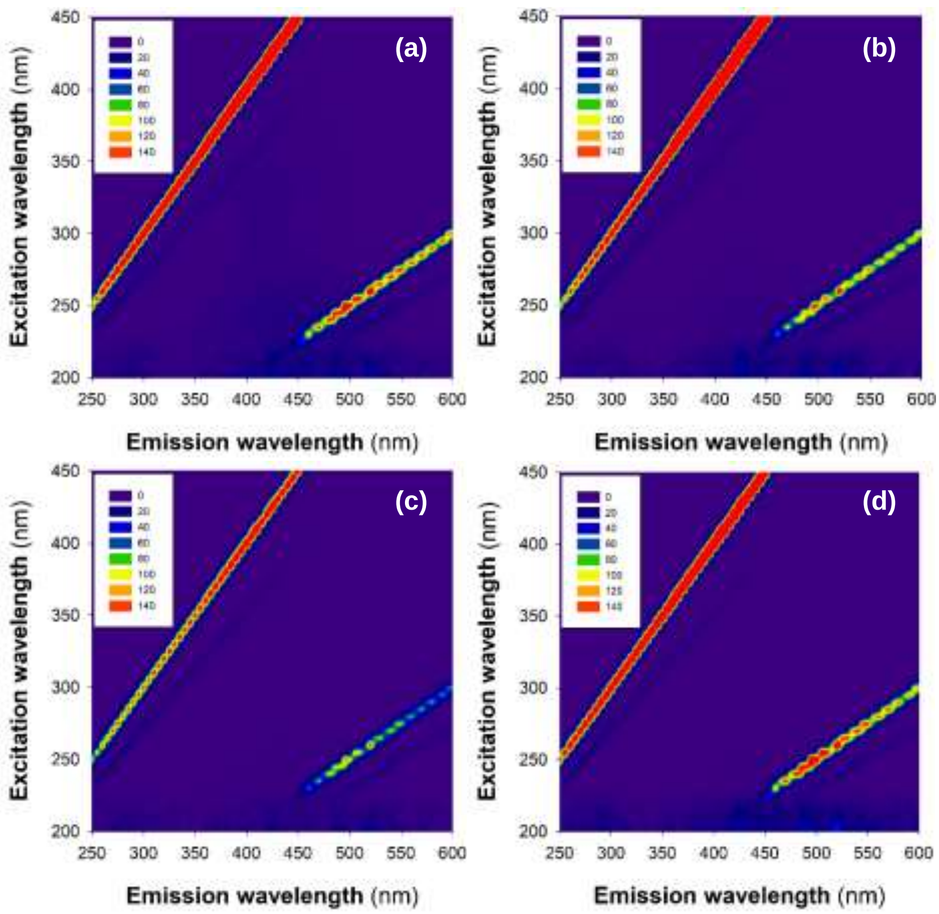

Figure S2. EEM spectra of Qian-an concentrate following (a) 30 min, (b) 60 min, (c) 120 min and (d) 180 min ozonation.

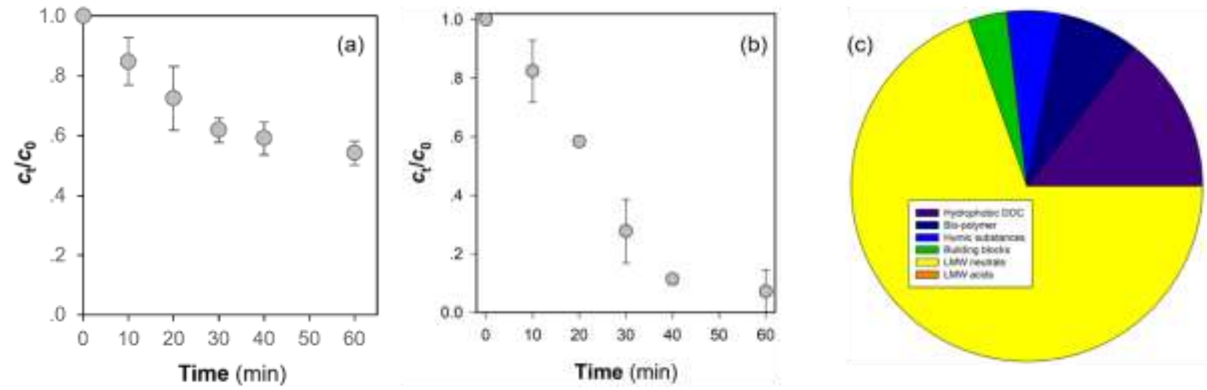

Figure S3. Measurement of DOC removal (a), COD removal (b) and change in LC-OCD components of humic acid (*i.e.*, humic substance) following 60 min of ozonation of 33 mg/L humics solution. $[DOC]_0$ = 33 mg/L; $[COD]_0$ = 79 mg/L ; [NaCl] = 51 mM ; $[Na_2SO_4]$ = 51 mM and $[NaHCO_3]$ =2 mM ;initial pH = 7.64.

S2: Techno-economic cost analysis

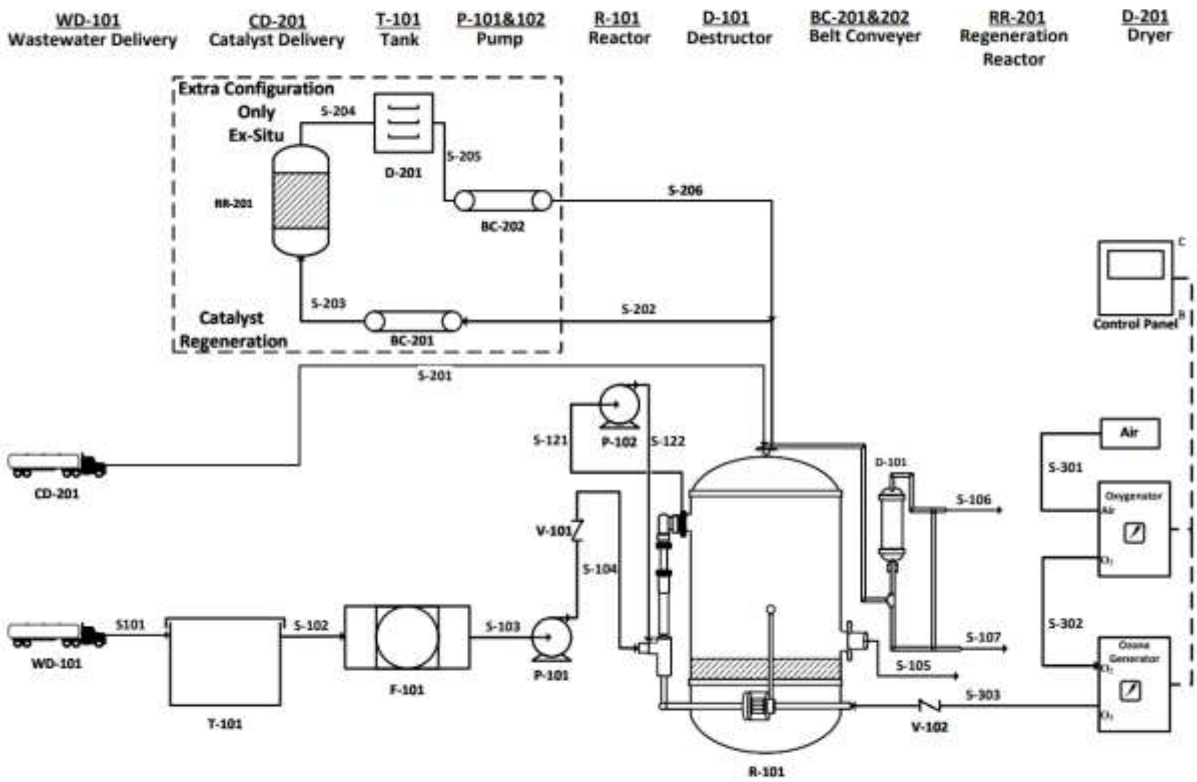

Figure S4. The process flow diagram for the ozonation and catalytic ozonation processes.

Using the process flow diagram shown in Figure S4, we calculated the total cost for the ozonation and catalytic ozonation processes. For fixed capital cost estimation, we included the inside battery limits (ISBL), offsite investment (OSBL), design and engineering and the contingency costs [1]. Firstly, the total purchase cost of the equipment (i.e. C_e), required for ISBL estimation, was calculated. The total capital cost of the equipment was estimated using the cost of the individual items of the process equipment. The cost of each piece of equipment is calculated using eq. S1 [3].

$$C_e = a + bS^n \qquad \text{(S2)}$$

where C_e refers to the purchased equipment cost calculated based on the reported parameter and prices in the US in Jan 2010 ; a and b refer to the cost constants of each equipment item, S is the size parameter, and n is the exponent for the equipment (see Table S3 for these parameters). The C_e value calculated using eq. S1 was then adjusted to the current cost of the equipment using the Chemical Engineering Plant Cost Index (CEPCI) which estimates the current cost based on the historical cost (eq.S2) [2, 3]

$$Cost_{current\ year} = Cost_{historical\ year} \times \frac{CEPCI_{current\ year}}{CEPCI_{historical\ year}} \quad \text{(S2)}$$

The current cost of each equipment and the total purchase cost is shown in Table S3. As shown, the total purchase cost of the equipment is \$1.02 M (or RMB 6.48 M) for a treatment capacity of 5000 m^3/d.

The ISBL was calculated using the total equipment purchase cost and various material factors reported earlier [3] employing eq. S3. The various material factors used for calculation are shown in Table S4.

$$\mathrm{C_{ISBL}} = \sum_{\mathrm{i=1}}^{\mathrm{1=M}} \mathrm{C_{e,i,A}}[(1 + \mathrm{f_p}) + (\mathrm{f_{er}} + \mathrm{f_{ei}} + \mathrm{f_i} + \mathrm{f_c} + \mathrm{f_s} + \mathrm{f_l})\ /f_m] \quad \text{(S3)}$$

The fixed capital cost was calculated using eq. S4.

$$\mathrm{C_{FC}} = \mathrm{C_{ISBL}}(1 + \mathrm{OS})(1 + \mathrm{D\&E} + \mathrm{X}) \quad \text{(S4)}$$

The total capital cost includes fixed capital cost and working capital.

Figure S5 shows the proportion of the fixed capital and total capital costs of the catalytic ozonation process. As shown, the ISBL cost accounted for most of the capital investment (~ \$2.33 M) while the contingency component constituted the lowest cost (~ \$0.09 M). Overall, the total capital costs (TCI) and fixed capital investment (FCI) of the catalytic ozonation process was estimated to be \$4.91 M (RMB 31.42M) and \$4.43M (RMB 28.35M), respectively.

Table S3. Equipment purchase cost for catalytic ozonation process

Capital Cost (USD & RMB)											
P&ID Number	Equipment	Material	Size	Unit	a	b	n	Quantity	Unit price (USD)	Cost (USD$)	Cost (RMB¥)
Cost for Equipment											
#	Oxygenator	NA($50\ Nm^3/hr$)	210*200*275	cm	NA	NA	NA	5	20,000	100,000	639,620
#	Ozone Generator	NA (2.5kg/hr)	1510*1220*1560	mm	NA	NA	NA	13	29,500	383,500	2,452,943
F-101	Filter	Canvas cloth	10	m^2	-73,000	93,000	0.3	1	0	130,184	833,178
S101-107,201-206,301-303	Double Pipe	Carbon steel	0.125	m^2	1,900	2,500	1	15	2,261	33,921	217,097
Cost for Tanks and Reactor											
T-101	Storage tank (wastewater)	Stainless steel	100	m^3	5,800	1,600	0.7	2	53,191	106,382	680,845
R101	Reactor (porcess)	Stainless steel/Titanium steel	50	m^3	NA	NA	NA	4	50,000	200,000	1,280,000
D-101	Ozone destructor (off-gas reactor)	Stainless steel	65*50*147	cm	NA	NA	NA	13	3,000	39,000	249,600
Cost for Pumps											
P-101	Wastewater pump	Stainless steel	2	m/s	8,000	240	0.9	1	8,518	8,518	54,515
P-102	Circulating pump	Stainless steel	2	m/s	8,000	240	0.9	1	8,518	8,518	54,515
Cost for Accessories											
V-101, 102	Check valves	Carbon steel	DN400	mm	NA	NA	NA	5	275	1,375	8,800
#	Flowmeter	Carbon steel/Stainless Steel	DN400	mm	NA	NA	NA	4	360	1,440	9,216
Plant capacity	$5000 m^3/day$	CEPCI 2010	532.9	Total purchased cost of the equipment						1,012,838	6,480,329
Feed COD (CW1#-4#)	150 mg/L	CEPCI 2020	607.8								
Effl. COD (designed)	50 mg/L	CEPCI 2021 (estimated)	616.34								
$O_3{:}COD_{removal} = 1.5{:}1$ $\quad O_2{:}O_3 = 10{:}1$											
$F_{Oxygen\ demand} = 218.67\ m^3/hr$ $\quad F_{Ozone\ demand} = 31.25\ kg/hr$											

Table S4 Typical factor for estimation of total capital cost

	Description	Value
$C_{e,i,A}$	Total equipment cost	\$1.02M ¥6.48M
f_{er}	Equipment erection	0.3
f_p	Piping	0.2
f_{el}	Electrical	0.2
f_i	Instrumentation and control	0.3
f_c	Civil	0.2
f_s	Structures and buildings	0.1
f_l	Lagging and paint	0.1
f_m	Materials cost factors	1
OS	Offsites	0.4
D&E	Design and Engineering	0.25
X	Contingency	0.1
	Working capital = 15% ISBL+OSBL	

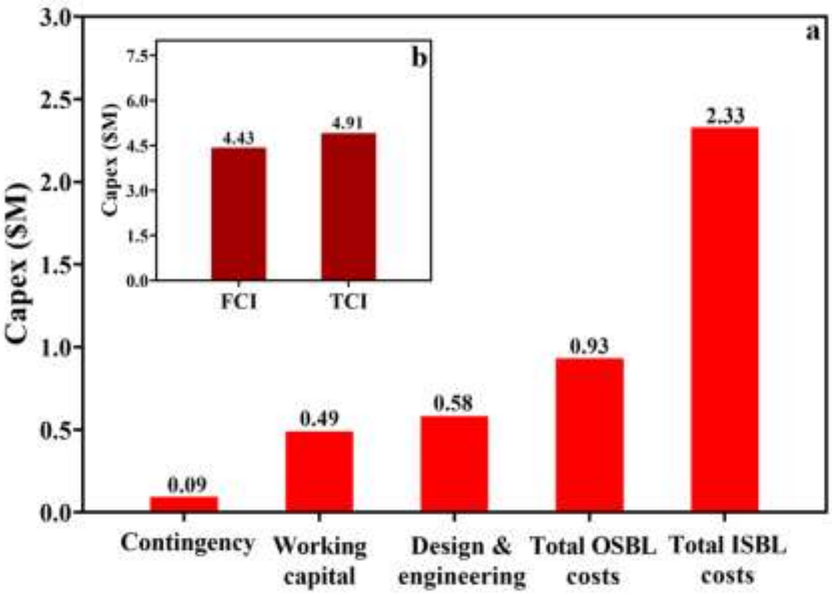

Figure S5. Total capital cost (TCI) and fixed capital cost (TCI) of the catalytic ozonation process.

For the operating cost calculation, we included raw material costs, transportation costs, utilities costs and waste disposal costs. Below we describe each of these costs:

(1) Raw material cost: The raw materials costs for the catalytic ozonation process mainly constitute the catalyst cost. Based on the treatment capacity of 5000 m^3/day of wastewater, volume of the process reactor and related degradation efficiency, 25 tonne of catalysts will be required for each reactor.

(2) Transportation cost: Operating costs of transportation was derived from the "Freight metrics truck operating cost calculator", and the related variables are listed in Table S5. Overall, the operating costs of transportation were determined using the current fuel cost (less any fuel rebate), vehicle selection, delivery amount, number of trucks required and driver wages.

(3) Utility costs: The main utility applied in the catalytic ozonation process was electricity since this wastewater treatment process does not require processing and cooling water. Normally, the electricity costs consist of two parts, including electricity applied on the equipment associated with the process and lighting plus office usage (TableS6). Based on an earlier report [4], the lighting and official usage accounts for around 5% ~ 30% of the total electricity consumption.

Table S5. Operating costs of raw material & transportation for catalytic ozonation process

Operating Costs (USD & RMB)					
Raw Material costs					
Raw Material	Quantity (t/reactor)	Unit Price (USD$/t)	Total Cost (USD$/t)	Total Cost (RMB ¥/t)	Ref.
Catalyst (Alum based)	25	2,000	200,000	1,280,000	https://www.made-in-china.com/
Transportation Costs					
Required variables for estimation		Value (US)		Value (China)	
Current fuel cost		USD$3.763		RMB¥30.749	https://www.globalpetrolprices.com/
The less fuel rebate (fuel credit)		USD$0.5		RMB¥NA	https://www.energy.gov/
Delivery amount & Truck number		100 tonne		100 tonne	
Truck driver wages		USD$30.77/hr		RMB¥52/hr	https://au.talent.com/ https://www.erieri.com/
Total operating costs (transportation)		USD$20,140		RMB¥118,590	https://freightmetrics.com.au/

Table S6. Operating costs (utility/annual) of catalytic ozonation process

Operating Costs (USD & RMB)					
Utility Costs					
Equipment	Power (KW)	Amount of units	Annual cost (USD$/)	Annual cost (RMB¥)	Ref.
Oxygenator	50	5	72,270	413,910	https://www.made-in-china.com/
Ozone Generator	16	13	60,128	344,373	
Filter	15	1	4,336	24,835	https://www.alibaba.com
Ozone destructor	10	1	2,890	16,556	https://www.valvesonline.com
Pump	13	2	7,516	43,047	http://www.oxo-auto.cz/
Lighting & official usage	Estimated as 15% of the total electricity usage		22,071	126,408	
Total utility costs			169,211	969,129	
*Average operating hours 8hr/day. Unit price of electricity = 0.11$/kWh & 0.63¥/kWh					
*Shutdown and maintenance coefficient =90%					

The total operating costs of the process were estimated to be $0.39M/annual (RMB 2.37 M/annual). The daily operating cost is $0.22/tonne (RMB 1.30/tonne) which is within the reasonable range. The higher operating cost is attributable to the higher raw material purchase cost (Figure S6).

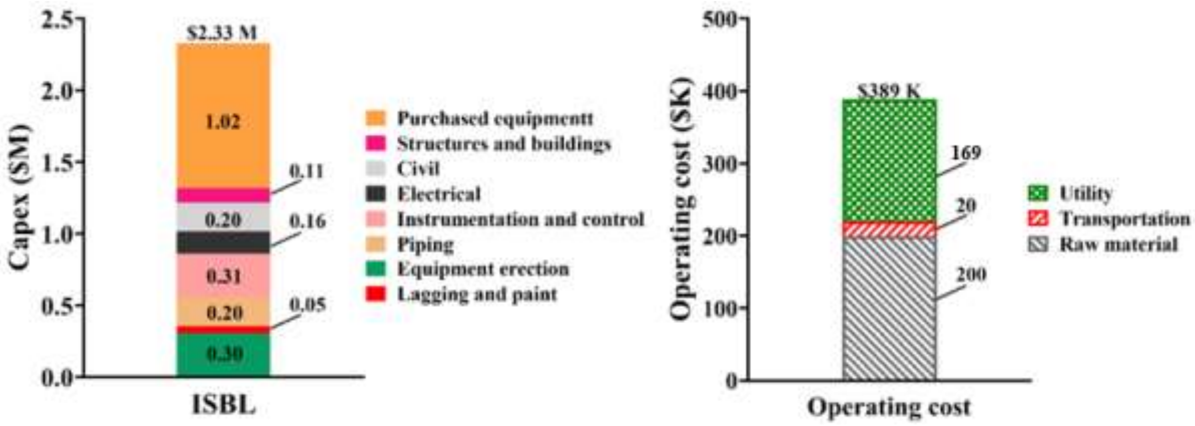

Figure S6. Share of ISBL and operating cost for the catalytic ozonation process.

S2.1 Cost of pure ozonation versus catalytic ozonation processes

The cost difference between the pure ozonation and catalytic ozonation processes is mainly reflected in the cost of raw material procurement, catalyst delivery and the extra process of catalyst regeneration (shown in Table S7). Usually, catalyst regeneration costs have not been included in previous analyses since the cost of this ex-situ configuration is a selective cost which is principally determined by the initial decision and enterprise demand.

Table S7 Total cost for extra configuration (catalyst regeneration)

Extra configuration (catalyst regeneration)											
Capital Cost (USD & RMB)											
P&ID Number	Equipment	Material	Size	Unit	a	b	n	Quantity	Unit price (USD)	Cost (USD$)	Cost (RMB¥)
BC-201&202	Belt conveyer	Rubber	100	mm	NA	NA	NA	2	2,000	4,000	25,600
RR-201	Regeneration reactor	Stainless steel	50	m^3	NA	NA	NA	1	50,000	50,000	320,000
D-201	Dryer	Stainless steel	3	m^2	10000	7900	0.5	1	23,683	23,683	151,571
S-(202-206)	Pipe	Carbon steel	0.125	m^2	1,900	2,500	1	5	2,213	2,213	14,160
Total capital cost = USD$79,896 (RMB¥511,331)											

Operating Cost (USD & RMB)						
Regeneration	Equipment	Power (Kw)	Usage hours (hr/batch)	Catalyst amount (tonne)	Cost (USD$)	Cost (RMB¥)
Regeneration	RR-201	1.520	3	100	127,070	515,000
Delivery	BC-201&202	18.7	3	100	165	943
Total operating cost = USD$127,235 (RMB¥515,943)						

References

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