

Optimal Design of a High Atom Utilisation and Sustainable Process for the Treatment of Crude Phenol Wastewater

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The high salt wastewater produced by crude phenol process is difficult to treat due to its high concentration of organics and salts. In this paper, the crude phenol process with replacement reactions is simulated with Aspen Plus to probe the wastewater generation process. A novel treatment process of high atom utilisation and sustainability is then designed to dispose of this wastewater, with the treatment effect analysed by experiment and simulation. In this treatment process, sodium carbonate is acidified by sulfuric acid, and the generated carbon dioxide is recycled back to the crude phenol process. Phenol is extracted from the wastewater, and sodium sulfate is further removed by electrolysis to obtain sodium hydroxide and sulfuric acid, which are used in the production of sodium phenolate and the acidification of sodium carbonate in crude phenol process. Because the proposed treatment process has a high atomic utilisation of carbon dioxide, sodium hydroxide, and sulfuric acid, it is a sustainable and economical process.

1. Introduction

Lignite contains a mass of phenolic compounds (Zhao et al., 2016), and the maximum economic benefits cannot be obtained by burning them directly (Meng et al., 2019). It is more economic when separating phenol from lignite and burning the other components as fuels. However, the separating process produces a wastewater stream containing high concentrations of phenol and sodium sulfate, which causes huge harm to the environment. The wastewater treated by oxidation or adsorption needs to be further treated to meet discharge standards. So, oxidation and adsorption are not the best methods to remove phenol from wastewater. Adenuga et al. (2019) proposed ternary Ag/AgCl/BiOCl as an alternative photocatalyst to realise the phenol degradation. However, the efficiency of phenol degradation is only 50 %, which is still far from that of extraction. Extraction is thus the main method to remove phenol. Currently, the researchers focus on selecting highly effective extraction solvents. For example, Olalla et al. (2019) proposed the deep eutectic solvents to remove phenol pollutant, and the extraction ratio of phenolic compounds is higher than 80 %. Guo et al. (2019) proposed the synergistic solvent consisting of methyl isobutyl ketone (MIBK) and n-pentanol (volume ratio 6:4) to achieve the removal efficiency to phenol up to 97.0 % using two-stage extraction. Cui et al. (2020) proposed the synergistic solvent consisting of methyl propyl ketone (MPK) and methanol to achieve the water mass fraction of treated wastewater up to 99.49 %. Another difficulty in disposing of such as wastewater is that it consumes a lot of energy to treat sodium sulfate wastewater by the evaporation process. The electrochemical method has become a hot spot to treat sodium sulfate wastewater because of its low-energy consumption. The sodium sulfate can be removed with the directional movement of charge based on electrolysis method (Ji et al., 2015). Tian et al. (2019) proposed the bipolar membrane electrolysis to treat hypersaline wastewater, and the sodium sulfate in wastewater was found decreasing from 8.0 % to 0.37 %. In this paper, a high atom utilisation and sustainable treatment process removing phenol and salt from wastewater is designed by extraction and electrolysis operations. The main contribution of this work consists in the effective treatment of wastewater along with higher economic efficiency.

realises the recovery and reuse of the synergistic extraction solvent, but also the additional supply of the sodium hydroxide and sulfuric acid to the production process by the electrolysis of sodium sulfate. The method thus obtains an increase in atomic utilisation.

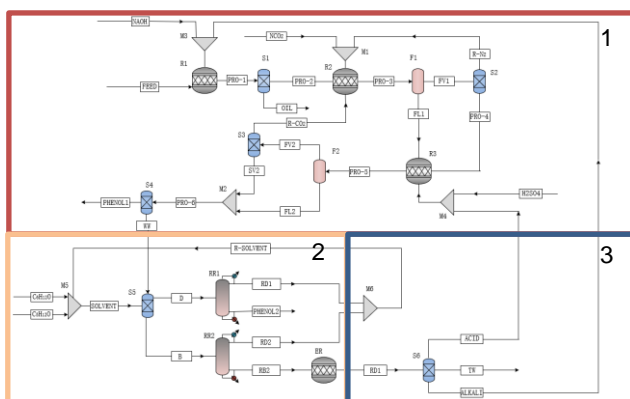


Figure 2: The treatment process of wastewater based on source process

In Figure 2, part 1 is the source generation process of wastewater. Part 2 is the process of dephenolization of the wastewater, in which the synergistic extractant is recovered from the distillation towers. Part 3 is the simulation of the wastewater electrolysis. The reusable sulfuric acid and sodium hydroxide are produced by electrolysis of sodium sulfate. Both partial and complete solution systems are involved in this paper. NRTL model is the liquid phase activity coefficient model. It can be applied to both two solution systems. Therefore, the NRTL model is used in the whole process.

3.1 Dephenolization of the wastewater

In Figure 2, part 2 is the simulation of removing phenol from wastewater. Block Extract is used as an extraction unit. The wastewater and synergistic extractant enter the extraction unit (S5) from the top and bottom to realise counter-current extraction. The synergistic extractant is composed of methyl isobutyl ketone (MIBK) with 1,433.59 kg/h and n-pentanol with 981.91 kg/h. The block RadFrac is used as a distillation operation for solvent recovery. RR1 is used to separate phenol and synergistic extractant in the extraction phase, and RR2 is used to separate a small amount of synergistic extraction solvent in the raffinate phase. The sensitivity analysis results of the number of stages for these two distillations are shown in Figure 3.

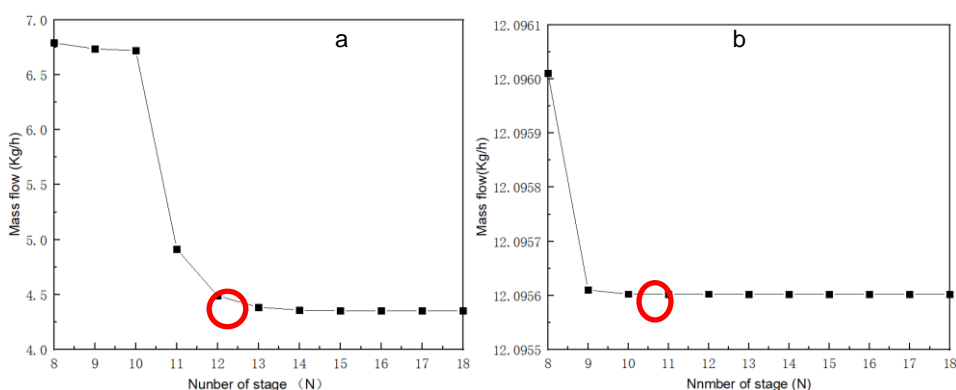


Figure 3: Sensitivity analyses of the number of stages

To separate phenols from synergistic extractant more effectively, the relationship between the number of stages in RR1 and the mass flow of MIBK in the bottom stream (PHENOL2) is analysed. Figure 3a shows the relationship between the number of stages in RR1 and the mass flow of MIBK in PHENOL2. The mass flow of MIBK in stream PHENOL2 decreases with the increase of the number of stages in unit RR1. When the number of stages is more than 12, the mass flow of MIBK changes slightly. However, the heat duty increases significantly. The number of stages for RR1 is finally determined as 12. Similarly, to separate water and synergistic extractant in raffinate more effectively, the relationship between the number of stages in RR2 and the mass flow of water in top stream (RD2) is analysed in Figure 3b. The number of stages for RR2 is determined as 10 in Figure 3b. The sensitivity analysis results of reflux ratio and bottoms to feed ratio of RR1 are shown in Figure 4.

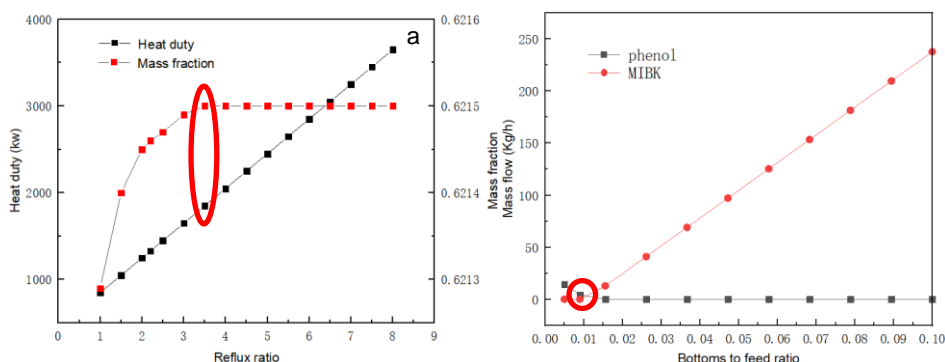


Figure 4: Sensitivity analyses of reflux ratio and bottoms to feed ratio of RR1

PHENOL2 is the phenol separated from the synergistic extractant. In order to recover more phenol from wastewater to improve the economic benefits, the changes of the heat duty of RR1 and the mass fraction of phenol in PHENOL2 with the increase of reflux ratio are shown in Figure 4a. It can be seen from Figure 4a that the mass fraction of phenol in stream PHENOL2 has no increase when the reflux ratio is larger than 3.5, but the heat duty increases significantly. Therefore, in order to reduce the operation costs, the reflux ratio of RR1 is set to 3.5. After the reflux ratio is determined, in order to separate phenol and MIBK better, the mass flow changes of MIBK and phenol in stream PHENOL2 with the bottoms to feed ratio up are studied in Figure 4b. When bottoms to feed ratio exceeds 0.009, the reduction of phenol is not obvious but the flow of n-butanol increases significantly. Therefore, without increasing the heat duty of RR1, the bottoms to feed ratio of RR1 is determined as 0.009. In the same way, unit RR2 reflux ratio is determined as 1.5, bottoms to feed ratio is 0.982. The parameters of the extraction unit and two solvent recovery units are listed in Table 3.

Table 3: The operation parameters of units S5, RR1, and RR2

Unit	S5	RR1	RR2
Solvent ratio	6:4	--	--
Number of stages (N)	4	12	10
Feed stage	--	6	5
Reflux ratio	--	3.5	1.5
Top flow / (kg/h)	2,472.41	2,447.02	113.18
Bottom flow / (kg/h)	3,270.81	25.40	3,157.64
Bottoms to feed ratio	--	0.009	0.982
Top temperature (°C)	25.31	81.66	78.47
Bottom temperature (°C)	23.56	157.03	101.13
Top pressure (bar)	1.013	1.013	1.013

Under the operating conditions listed in Table 3, the simulation result of the mass flow and fraction of wastewater and treated water are listed in Table 4.

Table 4: The mass flow and fraction of wastewater and treated water

	Mass flow (kg/h)		Mass fractions	
	WW	TW	WW	TW
C ₆ H ₆ O	15.77	7×10^{-4}	0.005	7.65×10^{-7}
H ₂ O	2,897.17	904.93	0.875	0.993
Na ₂ SO ₄	397.08	6.81	0.120	0.007

As can be seen from Table 4, the content of phenol in wastewater is significantly reduced as the mass flow is reduced from 15.77 to 7×10^{-4} by synergistic extraction and distillation. The mass flow and mass fractions of RD1 and RD2 are listed in Table 5.

Table 5: The mass flow and fraction of solvents in R1 and R2

	Mass flow (kg/h)		Mass fractions	
	RD1	RD2	RD1	RD2
C ₅ H ₁₂ O	944.94	27.37	0.41	0.36
C ₆ H ₁₂ O	1,385.0	48.56	0.59	0.64

In Table 5, streams RD1 and RD2 are synergistic extraction solvent recovered by distillation and can be reused in extraction block S5. The total flow of n-pentanol in RD1 and RD2 is 972.31 kg/h. The total flow of MIBK in RD1 and RD2 is 1,433.56 kg/h. Compared with the initial addition of MIBK and n-pentanol as the synergistic extraction solvent, the recovery rate of n-pentanol is 99 % and the recovery rate of MIBK is 99.9 %.

3.2 Electrolysis of the wastewater

The electrolysis of sodium sulfate is simulated based on the experimental data. The wastewater is prepared by dissolving 108.37 g sodium sulfate in 1 L distilled water. The operation conditions such as electrolysis time and current density influence the electrolysis of sodium sulfate. The optimal electrolytic operation condition is obtained by changing the parameters of the electrolytic tank. Mass fraction of sulfuric acid produced with different current density and time is shown in Figure 5.

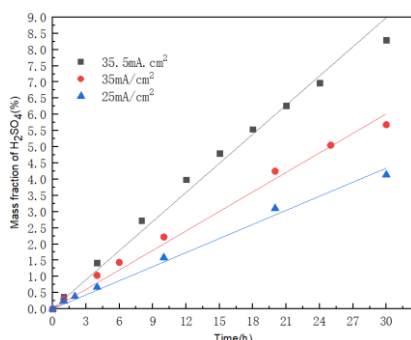


Figure 5: Mass fraction of sulfuric acid produced with different current density and time

In Figure 5, the mass fraction of sulfuric acid increases with the current density and time. When the electrolysis reached 30 hours, the mass fraction of sulfuric acid is 8.3 %, and that of sodium sulfate is 0.214 %. When continuously increasing the operating time, the mass fraction of sulfuric acid does not increase significantly, but the cost of electrolysis increases. So current density of 35.5 mA/cm² is selected to complete the electrolysis of sodium sulfate in this paper, and the electrolysis time is 30 h.

The mole concentration of sulfuric acid produced in acid compartment, sodium hydroxide produced in base compartment, and sodium sulfate consumed in salt compartment with time are analysed under the constant current density of 35.5 mA/cm², as shown in Figure 6.

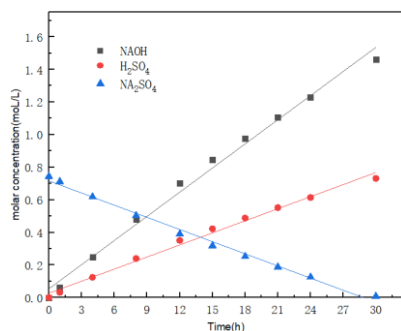


Figure 6: The molality varies of each component

In Figure 6, when the concentration of sodium sulfate decreases, the mole fraction of sodium hydroxide and sulfuric acid increases. The mole concentration expression of electrolysis results is shown in Table 6.

Table 6: The mole concentration expression of electrolysis experiment

Parameter	Expression	unit
$C_{H_2SO_4}$	$0.0247t+0.0274$	mol/L
C_{NaOH}	$0.049t+0.055$	mol/L
$C_{Na_2SO_4}$	$-0.025t+0.716$	mol/L

In Table 6, t is the time of electrolysis, $C_{H_2SO_4}$, C_{NaOH} , and $C_{Na_2SO_4}$ are the mole concentration of H₂SO₄, NaOH and Na₂SO₄. Based on the above experiment conclusions, the simulation results of the electrolysis process are shown in Table 7.

Table 7: The simulation result of the electrolysis process

	Mass flow (kg/h)		Mass fractions	
	ACID	ALKALI	ACID	ALKALI
H ₂ O	878.31	878.31	0.02	0.2
NaOH	0	219.79	0	0.8
H ₂ SO ₄	269.49	0	0.61	0

After 30 h of electrolysis, the final mole concentration of sodium sulfate is 1.84 g/L, the sulfuric acid is 71.64 g/L, and the sodium hydroxide is 58.48 g/L. As shown in part 3 of Figure 2, the blocks ER and S6 are used to simulate the electrolytic tank. The operating conditions are set by the experimental data. As an innovative wastewater treatment process, there is no industrial data to reference for the whole process. So only the wastewater electrolysis part which is difficult to model is explored experimentally, and the experimental results are compared with the simulation results. After 30 h of electrolysis, the experiment expressions show that the mass flow of sulfuric acid is 271.09 kg/h, and the mass flow of sodium hydroxide is 219.6 kg/h. Compare with the simulation results shown in Table 7, the data obtained from the experiment and the simulation are consistent. The relative error between the experimental data and the simulation results is less than 0.59 %, so the reliability of the simulation is verified.

4. Conclusions

The process established by Aspen Plus software realises the synergistic extractant recovery, along with the recycling of sulfuric acid and sodium hydroxide. The wastewater treatment process in this work reduces the amount of sulfuric acid and the corrosion of the equipment. A four-stage counter-current extraction is used to remove phenol from wastewater. The removal rate of phenol is 99.9 % when the mixture of MIBK to n-pentanol (volume ratio 6:4) is used as the synergistic extractant. After extraction, the electrolysis is used to reduce the sodium sulfate concentration. Operating conditions of the sodium sulfate electrolysis are determined by the experimental data. The combination of experiment and simulation makes the results of this paper more reliable. After the whole treatment, the mass fraction of sodium sulfate in the wastewater is 0.21 %, and the mass flow of phenol is 7×10^{-4} kg/h. In future work, the economic feasibility and the influence of salt concentration will be considered.

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