

Waste Water Treatment of Resorcinol Production

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Wastewater of resorcinol production that included acid, m-phenylenediamine, m-aminophenol, resorcinol, and other impurities was generated by m-phenylenediamine hydrolysis. In this paper formaldehyde condensed with organics of wastewater to form oligomeric solid polymer that could be separated by filtration. The oligomeric solid polymer could be used as plasticizer of rubbers. And then the acidity of wastewater was neutralized by adding ammonia water. It was found that other impurity reacted with ammonia and precipitated from the solution in the neutralized process. Methanol and n-butyl ester of wastewater were removed by stripping one third water after forward two steps. Lastly activated carbon was utilized to adsorb trace organics and impurities, and then water was evaporated to product ammonium sulphate. An orthogonal experiment about adsorption temperature, activated carbon quantity, stirring time was arranged to gain optimal activated carbon adsorption operation conditions. The condensed mole ratio of formaldehyde and organics, neutralized pH value, and the activated carbon adsorption conditions were investigated to achieve the minimum impurities, the qualified nitrogen content, and the best color of ammonium sulphate. The final mole ratio of formaldehyde and organics was 4:1 according to the minimum organics residues and the best color of ammonium sulphate product. At the neutralized pH value of 7 ~ 8, the color and nitrogen content were optimal and the ammonium sulphate had a little impurities. Based on the range analysis results of orthogonal experiment and the color of ammonium sulphate, the minimum impurities and best color of ammonium sulphate were at adsorption temperature of 90 °C, activated carbon quantity of 3 %, the stirring time of 30 min. The evaporated water vapor can be condensed and reused as process water to minimize the wastewater discharge of the production process.

1. Introduction

Resorcinol is a fine chemical material, which is widely applied to rubber additive, pesticide, medicine etc. It can be synthesized by alkali fusion of meta-benzenedisulfonic acid, the hydroperoxidation of meta-diisopropylbenzene, or the hydrolysis of meta-phenylenediamine. The hydrolysis of meta-phenylenediamine is a one-step reaction with the advantage of less pollution and less by-product (Durairaj and Jesionowski, 2003). For all that, wastewater still produced when hydrolysate was separated by extraction (Matsunaga et al., 1987). It was acid reddish brown and contained resorcinol, m-phenylenediamine, m-aminophenol and other impurities. Resorcinol and m-aminophenol are toxic and have been classified as hazardous pollutants because of their potential harmfulness in human health (Wu et al., 1997). M-phenylenediamine is harmful to public health and environment due to its toxicity and carcinogenicity (Laha and Luthy, 1990). Acid wastewater corrodes sewer pipe, hydro-structure, factory building foundation and damages aquatic organisms, crops. Therefore, proper treatment is necessary to remove phenols and aniline of wastewater before discharge.

Available methods for removal of phenols from resorcinol wastewater include activated carbon adsorption (Caturla et al., 1988), solid-phase extraction (Masque et al., 1998), emulsion liquid membrane (Balasubramanian and Venkatesan, 2012), electrocoagulation (Adhoum and Monser, 2004), chemical oxidation (Namasivayam and Sumithra, 2007), peroxidase treatment (Caza et al., 1999), activated sludge process (Mulas and Skogestad, 2005). There are many studies regarding the different alternatives that exist to treat wastewaters polluted with aniline, such as adsorption (Xie et al., 2007), extraction (Qi et al., 2002), biodegradation (Jiang et al., 2016), oxidation (Anotai et al., 2006). However, these traditional treatment

methods of phenols and anilines may suffer from serious drawbacks as high cost, complex operation, secondary pollution, incomplete removal and applicability to a limited concentration range. So it is beneficial to find a new treatment method that is low cost and feasible.

To our knowledge, novolac phenolic resins are produced by the acid-catalysed condensation polymerization of phenols with aldehyde (Aranguren et al., 1984). And aniline formaldehyde condensate can be easily synthesized by the polymerization of aniline in presence of formaldehyde in acidic medium (Koner et al., 2008). So the condensation reaction is a good pretreated method in selective removal of phenols and aniline. Novolac phenolic resin was synthesized using phenol and formaldehyde when the mole ratio of formaldehyde-phenol was 1.67:2 with the presence of dilute sulphuric acid and stirring at 100 °C (Chiang and Ma, 2004). In other paper, different colour resorcinol-formaldehyde gels were synthesized using formaldehyde and resorcinol of different mole ratios in hydrochloride catalysing and presence of acetonitrile, which was completed in about 2 h at room temperature or in 10 min at 80 °C (Mulik et al., 2007). Aniline formaldehyde condensate also was synthesized using aniline and formaldehyde with hydrochloride catalyzing and intermittent stirring at 80 °C for 2 h (Kumar et al., 2007). Simply, acid water can be treated by neutralization (Gordon and Malachosky, 1997).

In this work, the treatment of m-phenylenediamine hydrolysis wastewater includes three main steps. Firstly, organics of the wastewater react with formaldehyde and the precipitation is removed by filtration. Secondly, the wastewater is neutralized by ammonia water and ammonium sulphate is produced. Finally, a spot of impurities and colour are treated by activated carbon. Qualified ammonium sulphate is obtained by evaporating water. The evaporated water can be condensed and reused as process water.

2. Experimental section

2.1 Chemicals

Wastewater was from the factory and the composition was shown in Table 1. In the composition, the structure of impurity 1 was unknown. Formaldehyde (37 % HCHO) was purchased from Shandong Dino Chemical Co., Ltd. Ammonia water (25 % NH₃) was purchased from Tianjin Xiangruixin Chemical Technology Co., Ltd. Powdered activated carbon (AR) was from Tianjin Xiangruixin Chemical Technology Co., Ltd.

Table 1: Composition of wastewater.

Name	M-phenylenediamine /ppm	M-aminophenol /ppm	Resorcinol /ppm	Impurity 1 /ppm	Concentration of hydrogen ion (sulphate representation)
Content 77	77	500	2,220	570	10.02%

2.2 Instruments

Phenolic reaction was performed in three mouth flasks with condenser tube, thermometer and agitator. Precipitation was filtered by decompress filter that was composed of Buchner funnel, filter flask, vacuum pump (2XZ-2, Zhejiang taizhou qijing vacuum pump co., Ltd) with motor (YC7134, Wenling suli motor factory).

The content of m-phenylenediamine, m-aminophenol, resorcinol and impurity was analysed by HPLC system of Dionex (P680 HPLC Pump, Thermostatted Column Compartment TCC-100). Nitrogen content of ammonium sulphate was measured by formaldehyde method (Song, 2003).

2.3 Experimental method

2.3.1. Amount of condensation formaldehyde

The reaction was performed in three mouth flask with condenser tube, thermometer and agitator. The total amount of organics in the wastewater was measured. The reagents, formaldehyde and wastewater were added to three mouth flask according to the certain mole ratio of formaldehyde and organic compounds. The reaction was proceeded at 40 °C. During the reaction, about 10 g reaction solution was taken out to be analysed by HPLC hourly. The reaction was maintained until the content of resorcinol did not decrease. Table 3 was the analysis result of final sampling. The content of residual formaldehyde was measured after the end of the reaction. Then filtrate was obtained by filtration and was weighed. Then, ammonia water was added to filtrate to adjust the pH to 7~8 and the quantity was recorded. Precipitation was filtered. After the filtration, methanol and n-butyl ester were removed by evaporating one third water. Precipitation was filtered and filtrate was weighed. Lastly, enough activated carbon was added to adsorb for 30 min. This was followed by filtration and weighing. After weighing, ammonium sulphate was obtained by evaporating water. The nitrogen content of ammonium sulphate was determined by formaldehyde method and impurity content of ammonium sulphate was analysed by HPLC. The analysis results were shown in Table 4. The mole ratio of formaldehyde and

organics was changed and experiment was continued. The optimal formaldehyde quantity was determined by the highest purity and the best colour of ammonium sulphate.

2.3.2. Neutralized pH

Under optimal formaldehyde amount, condensation reaction was carried out for 2 h at 40 °C. About 1,000 mL filtrate was obtained and divided into 3 portions. Every portion was about 300 mL. The pH value of 3 portions filtrate was adjusted to 5 ~ 6, 6 ~ 7, 7 ~ 8. Precipitation was filtered. One third water was evaporated to remove methanol and n-butyl ester. Precipitation was filtered and filtrate was weighed. 1 % activated carbon was added to adsorb for 30 min. The adsorbed activated carbon was removed by filtration. The nitrogen content and impurity content were analysed to determine the neutralized pH value. The analysis results were shown in Table 5.

2.3.3. Activated carbon adsorption

The wastewater was pretreated with above mentioned condensation and neutralization. An orthogonal experiment with three factors and three levels about adsorption temperature, activated carbon quantity and stirring time was designed. The factors and levels of orthogonal experiment were shown in table 2. The specific array of orthogonal experiment was shown in table 6. The optimal adsorption conditions were determined by the range analysis of impurity 1 content, resorcinol content and the color of ammonium sulphate.

Table 2: Factors and levels of orthogonal experiment.

Level	Factor		
	Temperature/°C	Amount of activated carbon/%	Stirring time/min
1	60	1	10
2	75	3	30
3	90	5	50

3. Results and discussion

3.1 Determination of formaldehyde quantity

Table 3 is the content of liquid residual organics after formaldehyde organics condensation experiment of different mole ratio.

Table 3: Liquid residual organics results after formaldehyde organics condensation of different mole ratio.

		M-phenylenediamine /ppm	M-aminophenol /ppm	Impurity 1 /ppm	Resorcinol /ppm
Wastewater		77	500	570	2,200
10:1	1	0	0	510	7
	2	0	0	520	6
	3	0	0	460	7
8:1	1	0	0	500	17
	2	0	0	500	16
	3	0	0	450	6
6:1	1	0	0	550	3
	2	0	0	520	1
	3	0	0	500	1
4:1	1	0	0	500	19
	2	0	0	520	2
	3	0	0	510	1
3:1	1	0	0	500	29
	2	0	0	500	12
	1	0	15	580	0
2:1	2	0	11	494	0
	3	0	0	498	0
	1	0	59	610	1,375
1:1	2	0	23	488	0
	3	0	2.3	530	0
		0	0	68	102
Ammonia water neutralization		0	0	68	102

From Table 3, it is found that the m-phenylenediamine can react with formaldehyde completely. When the mole ratio of formaldehyde and total organics is less than 3, m-aminophenol can be detected even the reaction time is 2 h. Otherwise, m-aminophenol can be eliminated when the mole ratio of formaldehyde and total organics over above value. It indicates the m-aminophenol needs enough formaldehyde to be removed completely.

Impurity 1 existed in the original water. The impurity 1 decreases very small when formaldehyde is added from Table 3. This implies impurity 1 is not affected by formaldehyde. The result of last row of Table 3 was determined by the condition that pH value is adjusted to 7~8 after formaldehyde-organics 10:1 condensation. It is found that impurity 1 greatly decreases after adding ammonia water from the result.

From Table 3, the content of resorcinol decreases to lower content after adding formaldehyde. This implies the large amount of resorcinol can be removed by using formaldehyde. The 1:1 formaldehyde-organics mole ratio is enough for removing resorcinol.

Ammonium sulphate is obtained by evaporating water after neutralization and adsorption. To obtain qualified ammonium sulphate and the optimal formaldehyde-organics mole ratio, the nitrogen content, impurities content and colour of ammonium sulphate are used as indexes.

Table 4: The characteristic of ammonium sulphate under different mole ratio.

Ratio	Nitrogen content /%	Resorcinol /ppm	Impurity1 /ppm	Color
10:1	20.76	2	2	light yellow
8:1	21.07	3	3	light yellow
6:1	20.97	2	3	light yellow
4:1	21.04	3	3	white
3:1	21.10	7	5	white
2:1	21.07	8	10	white
1:1	20.96	13	21	white

Table 4 is the analysis results of ammonium sulphate product under different formaldehyde-organics mole ratio.

As is known, the required nitrogen content of qualified ammonium sulphate is 20.5 %. Table 4 shows that nitrogen content of all mole ratios is satisfied. It suggests the nitrogen content is qualified if the formaldehyde is sufficient to react with organics. The impurities quantity of ammonium sulphate is less when the mole ratio of formaldehyde and total organics is greater than 3. However, the colour of ammonium sulphate changes to yellow if the mole ratio is greater than or equal to 6. According to the residual m-aminophenol content of liquid phase and the impurities content and colour of ammonium sulphate, the optimal condensation mole ratio of formaldehyde and organics is 4.

3.2 Determination of pH value

Table 5 is the analysis results of ammonium sulphate of different pH value after formaldehyde organics condensation.

Experiment results in Table 5 show that the nitrogen content of ammonium sulphate is qualified under the three pH values. And the content of resorcinol impurity of ammonium sulphate is a little at the three pH values. The colour of ammonium sulphate is all white under the three pH values, too. The content of impurity 1 decreases with the increasing basicity. It is sure that the impurity 1 can be removed by adding ammonia water. And ammonium hydrogen sulphate can be guaranteed to transform into ammonium sulphate at pH 7 ~ 8. To maintain minimum impurities content of ammonium sulphate and the best ammonium sulphate, the optimal neutralized pH value is determined to 7 ~ 8.

Table 5: Analysis result of ammonium sulphate of different pH value.

	pH=5~6	pH=6~7	pH=7~8
Color	white	white	white
Nitrogen content/%	21.14	21.17	21.19
Content of resorcinol impurity /ppm	2	0	2
Impurity 1 /ppm	204	87	62

3.3 Determination of activated carbon quantity

Table 6 shows the color, nitrogen content, resorcinol content and impurity 1 content of ammonium sulphate of different factors at different levels.

Table 6: Results of orthogonal experiment.

Experiments	Experimental conditions	Color	Nitrogen content	Resorcinol content/ppm	Impurity1 content/ppm
1	60 °C、1 %、10 min	light yellow	20.51 %	12	208
2	60 °C、3 %、30 min	white	20.82 %	4	104
3	60 °C、5 %、50 min	white	19.91 %	5	248
4	75 °C、1 %、30 min	light yellow	20.89 %	8	110
5	75 °C、3 %、50 min	white	20.81 %	9	86
6	75 °C、5 %、10 min	white	20.06 %	7	323
7	90 °C、1 %、50 min	light yellow	21.11 %	1	7
8	90 °C、3 %、10 min	white	20.79 %	1	107
9	90 °C、5 %、30 min	white	21.05 %	0	11

Table 7: Range analysis of resorcinol content of ammonium sulphate.

	Temperature	Amount of activated carbon	Stirring time
K ₁	7.000	7.000	6.667
K ₂	8.000	4.667	4.000
K ₃	0.667	4.000	5.000
R	7.333	3.000	2.667

Table 7 shows the resorcinol content range analysis result of every factor. As is known, the range value (R) indicates the significance of the factor's effect and a larger R means the factor has a bigger impact on the index. Therefore, compared with the range values of different factors (R), the factors' levels of significance are as follows: temperature > amount of activated carbon > stirring time. From table 7, the optimal adsorption conditions are temperature factor 3 (90 °C), amount of activated carbon factor 3 (5 %), stirring time factor 2 (30 min). This suggests high temperature and large amount of activated carbon are useful to adsorption.

Table 8: Range analysis of impurity 1 content of ammonium sulphate.

	Temperature	Amount of activated carbon	Stirring time
K ₁	186.667	108.333	212.667
K ₂	173.000	99.000	75.000
K ₃	41.667	194.000	113.667
R	145.000	95.000	137.667

Table 8 is the result of impurity 1 content range analysis of every factor. Compared with the range values of different factors (R), the factors' levels of significance are as follows: temperature > stirring time > amount of activated carbon. From the table 8, the optimal adsorption conditions are temperature factor 3 (90 °C), amount of activated carbon factor 2 (3 %), stirring time factor 2 (30 min). This suggests high temperature is useful to adsorption.

From range analysis results of resorcinol content and impurity 2 content of ammonia sulphate, there is only the activated carbon quantity different among optimal conditions. However, 3% activated carbon quantity is enough according to the colour of ammonium sulphate from table 6.

The optimal activated carbon adsorption conditions are 90 °C, 3 % activated carbon, 30 min stirring time. And high temperature is useful to adsorption from the optimal conditions.

4. Conclusion

The optimal mole ratio of formaldehyde and organics is 4. The reaction rate is slow when amount of formaldehyde is less than this value and the colour of ammonium sulphate is too deep when amount of formaldehyde is greater than this value. The nitrogen content of ammonium sulphate is qualified at three pH values. The impurity 1 of ammonium sulphate decreases with the increasing ammonia water. And ammonium

hydrogen sulphate can be guaranteed to transform into ammonium sulphate at pH 7 ~ 8. The optimal pH value is 7 ~ 8. The optimal activated carbon adsorption conditions are 90 °C, 3 % activated carbon, 30 min stirring time according to the discussion results of orthogonal experiment. The colour and nitrogen content of ammonium sulphate is qualified. The impurity quantity of ammonium sulphate is accepted, too. The evaporated water vapor is condensed and reused as process water, which can minimize the wastewater discharge of the production process.

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