ISSN : 0974 - 7435 Volume 10 Issue 18

2014

BioTechnology

An Indian Journal

FULL PAPER

BTAIJ, 10(18), 2014 [10220-10223]

The azeotropic behavior of waste water that contains phenol and high concentrated salt in a distillation column

Wenze Li[1,2], Shaoqing Chang[2], Xuan Qi[2], Depeng Liu[2], Chao Zhang[2], Hong-bin Sun[2]*

[1]College of Applied Chemistry, Shenyang University of Chemical Technology, Shenyang 110142, (P.R.CHINA)

[2]College of Science, Northeastern University, Shenyang 110819, (P.R.CHINA)

E-mail : sunhb@mail.neu.edu.cn; kent.qx@163.com

ABSTRACT

The waste water containing phenol and high concentrated sodium chloride is treated by distillation. Applying a distillation tower, more than 99% phenol is recycled by azeotropic batch fraction. The reflux ratio is optimized to 3 when a fraction column with ten theoretical perfect plates is used. Comparatively, the simple distillation gives dissatisfactory removal of phenol from the waste water.

KEYWORDS

Waste water; Phenol; Recycling; Azeotropic distillation; High concentrated NaCl.

The treatment of waste water is a popular topic in environment science. The phenol contained waste water, which is produced in a lot of manufactory procedure, is being concerned very much because it is harmful and difficult to handle by common water treatment process. The biological sewerage, which is the general useful method for waste water, meets difficulty as phenol is toxic to most microbes that used in the treatment procedures. Especially when the waste water contains a high concentrated inorganic salt, for example sodium chloride, the biological treatment almost does not work because the usual microbe can't live in such environment. But this type of waste water is generating everyday in the manufactory of pesticides, dyes, and other chemicals. It is uneconomical to extract few thousandths of phenol from water for the loss of extraction solvent, and the residual solvent should be get rid of by another way.

Therefore, a lot of practice techniques are carried out to handle the phenol contained waste water, including solvent extraction[1], absorption[2], steam distillation, chemical oxidation[3], electrochemical oxidation[4,5], biochemical treatment[6] and emulsion extraction. For example, Cheng *et.al* have reported an emulsion extraction of waste water from the production of 2, 4-dichloroacetic acid and 2-methyl-4-chloroacetic acid[7,8], and Huang et.al[9] have reported a distillation-extraction treatment of o-cresol contained waste water. The two reports are about extraction method. Due to the extraction efficiency, the residual organics in the water is remained. Besides the extraction, in every progress, the phenol is removed from water with certain degree. The thorough harmlessness of waste water often needs a combination of different methods. In this paper, we report an improved steam distillation to the treatment of phenol contained waste water, azeotropic batch fraction. This method is very suitable to waste water that contains high concentrated salt.

The boiling point of phenol is 181.9 ^{o}C, and pure water is 100 ^{o}C. From the two component phase diagram, we can find that the phenol and water azeotrope at 99.5 ^{o}C with 9.2 percent of phenol in the gas phase mixture. But the azeotropic temperature is too close to the pure water's boiling point that the phenol can't be separated entirely from water by simple distillation. Although phenol azeotropes with water, but because of the low concentration, the amount of phenol that is distilled to gas phase is very small, so a large excess of steam is often needed to get rid of residual phenol. This is wasteful and uneconomical. Even general fraction distillation can't work properly while a low concentration of phenol is loaded. Such a separation requires a high enough tower with large operational reflux ratio. However, we found that a batch fraction distillation can do this work without critical equipment.

The experiments are carried out in a glass distillation tower that is composed of a 2000 mL round bottom flask, a fraction column of 1000 mm long and 50 mm inner diameter packed with 4 mm ceramic ring, and an inner-reflux head with a reflux ratio controller. The fraction tower is determined with a cyclohexane-heptane system. Total reflux a 1:1 (mole ratio) cyclohexane with heptane mixture in the tower, then the upper and bottom composition are determined. The number of theoretical plates is calculated by the Fenske equation (1). The x_w means bottom concentration, and the y_l means upper concentration, and the $_m$ means average relative volatility calculated by Antoine equation.

$$N = \frac{\lg[(\frac{y_l}{1-y_l})(\frac{1-x_w}{x_w})]}{\lg \alpha_m} - 1 \qquad \textbf{(1)}$$

By this method, the theoretical plate number is determined to be 10. The experimental waste water is made of 5 g of phenol, 200 g of sodium and 1000 g of water. The waste water is added to the bottom of the distillation tower then heated, after reflux for 1 hour to establish tower equilibrium, the reflux ratio controller is switched on to start distillation. The fractions are collected every 10 mL as samples, then the samples are analyzed by HPLC to determine the phenol concentration. There are 15~20 samples are collected before the distillation is terminated. The reflux ratio is changed in different runs. We found the suitable reflux ratio is 3:1.

During the distillation, the phenol and water in the bottom is evaporated constantly, but the upper phenol concentration is quite different with the bottom. Because the phenol and water formats an azeotrope mixture, with the improvement of the column efficiency, the upper concentration of phenol raises to approach 9.2 wt%, which is the theoretical value. In our 10 theoretical plates refining column, the initial upper concentration is 5%~ 8% phenols at different reflux ratio. The initial upper concentration is the highest one during the distillation, and then the upper concentration drops with the remove of phenol. The distillation with 3:1 reflux ratio is illustrated as Figure 1. We find that the batch distillation can be divided into three stages. In the first several samples the phenol evaporates with almost constant composition (region *a*), after that stage the upper concentration begins to drop. This is the second stage (region *b*). The mainly phenol evaporates to the gas phase in the first two stages. After that, the amount of the residual phenol in the bottom is very small. After the third stage (region *c*) distillation, the bottom phenol concentration is so low that its signal in HPLC is not larger than the background noise in the absence of extraction and concentration. The upper and bottom concentration gets near and near as the distillation progresses, so the separation of phenol becomes difficult in the third stage.

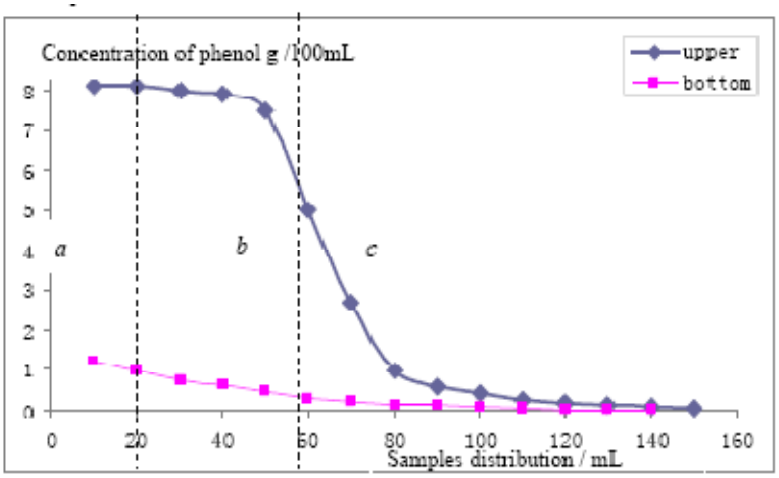

Figure 1 : Fine distillation of phenol-containedwaste water with 3:1 reflux ratio

In the initiate experiment, we used a 3:1 reflux ratio during the distillation. After establishing the tower balance, the fraction evaporated from the top of the column is collected every 10 mL as samples. The first 10 mL of mixture is treated as the initial sample. It contains 81 g/L of phenol. In the following several samples, the concentrations drop very slow so as to draw a "platform" in the distillation progress Figure as region *a* (Figure 1). There is still 79 g/L phenol in the fourth sample. Operating along the platform area of the curve, 3.2 g of phenol is collected on the top of the column. That is over 60% of total added phenol. From the fifth sample, the upper concentration begins to drop. It drops quickly to less than 10 g/L after 3 samples. The fast-drop period draws the region *b*. After that, the distillated phenol in fraction maintains a smooth reduction. That draws the region *c*. Being different to the upper sample, during the distillation, the bottom samples draw a smooth decrease curve of the phenol's concentration with time. We can find from the distinctive curve that if the main purpose is to recycle phenol, the distillation can be cancelled after *a* region. At this time, the phenol's concentration in the bottom is 460 mg/L (less than 10% of starting water). Distillation in this way consumes the lowest energy; otherwise the operation should be stopped after *b* region, while the phenol in the bottom is 80 mg/L, at this time over 96% of phenol is recovered. If the main goal is to remove phenol entirely, the operation should be performing to *c* region so as to lower the phenol concentration to less than 2.5 mg/L. But in this way the energy consumption is great.

The experiments are carried out at different conditions by changing the reflux ratio to 2:1, 4:1 and 5:1. The similar results are obtained in the experiments of 4:1 and 5:1 reflux ratio, but there are some differences in details, especially when the operation is carried out at the reflux ratio of 2:1. The results are summarized in TABLE 1.

TABLE 1 : Distillation of phenol containedwaste water in fraction tower with different reflux ratio

Reflux ratio	Phenol recycled in 15 samples	Residual phenol (mg/L)	Platform sample number	Initial upper concentration (g/L)
2:1	82.8%	90	2	60
3:1	99.5%	2.5	4	81
4:1	99.0%	2.4	4	82
5:1	99.3%	2.3	4	79

The experimental phenomenon is explained as follows. Due to phenol and water azeotrope, if the column efficiency is good enough, the upper fraction can reach the theoretical composition ratio. Therefore, when the bottom concentration is high enough, the upper concentration there will be "saturated" to perform a stable value. With the phenol is constantly evaporated, the concentration of the bottom quickly reduces, and the concentration of the top of the tower also decreases. The remaining phenol in the body of the tower phenol is brought out with steam to become the *b* region of Figure 1. Still later, the tower changes in the concentration of the top and bottoms tend to be similar. With the reflux ratio is increased from 2:1 to 3:1, the tower efficiency increases, so the phenol concentration in initial fraction is increased. The number of "saturated sample" is also increased, so the length of platform area is increased. But in the experiment with reflux ratio 4:1 and 5:1, due to the limitations of the tower itself, the column efficiency have been no significant improvement, therefore they give similar results to the 3:1 reflux ratio.

In summary, we find that refine distillation is a possible way to handle the waste water that contains phenol and high concentrated salt. By using a 10 theoretical plates refine column and operating at reflux ratio 3:1, 99.5% phenol can be recycled from the top of the column while the collection is 15% to the total amount of waste water. And the residual phenol

in the bottom waste water is less than 0.5%. Otherwise, if the main goal is to recycle phenol in a energy-efficient way, the operation could be terminated after 5% of waste water is distillated.

ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (21003018) and the Doctoral Starting up Foundation of Liaoning Province (20121071) are gratefully acknowledged.

REFERENCES

[1] C.Hanson; Recent advances in liquid-liquid extraction, Oxford：Pergamon Press, 67-74 **(1977)**.

[2] P.E.Diaz-Flores, R.Leyva-Ramos, R.M.Guerrero- Coronado; Adsorption of pentachlorophenol from aqueous solution onto activated carbon fiber. *Ind. Eng. Chem. Res.*, **45(1)**, 330-336 **(2006)**.

[3] C.W.Yang, W.H.Zhai, Y.Cai, H.J.Li; Dynamics study of Fenton advanced oxidation of phenol. *Heilongjiang Environmental Journal*. **33(3)**, 70-74 **(2009)**. (in Chinese)

[4] L.F.Qiu, E.L.Ni; Preparation of dimensionless stable anode in the electro-catalytic oxidation and its phenol- degrading characteristics. *Environmental Chemistry*, **29(6)**, 1019-1026 **(2010)**. (in Chinese)

[5] W.Z.Cheng, M.H.Zhou; Partial degradation of phenol by advanced electrochemical oxidation process. *Environ Sci Technol*. **35(13)**, 2698 -2703 **(2001)**.

[6] P.Kumaran, Y.L.Paruchuri; Kinetics of phenol biotransformation. *Water Research*, **31(1)**, 11-12 **(1997)**.

[7] D.Cheng, P.Li, S.J.Xu, W.J.Ma, Y.C.Ou; CN 201110009946.0

[8] D.Cheng, P.Li, S.J.Xu, W.J.Ma, Y.C.Ou; CN 201110020660.2

[9] J.Z.Huang, W.W.Liao, Z.L.Liu; Studies on Waste Water of o-Cresol Pilot Test. *Hubei Hua Gong*, **1**, 13-14 **(1999)**. (in Chinese).