Recovery of Aniline from Wastewater by Nitrobenzene Extraction Enhanced with Salting-Out Effect[1]

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Objective Nitrobenzene extraction enhanced by salting-out effect was employed to recover aniline from wastewater at 25 ℃. **Method** Batchwise experiments were conducted to elucidate the influence of various operating variables on the extracting performance, including acidity of wastewater, initial aniline concentration, ratios of solvent to wastewater, extraction stages, concentrations and different types of inorganic salts, such as NaCl, KCl, Na_2SO_4, $CaCl_2$ and K_2SO_4. **Results** Nitrobenzene with a concentration of 20% and a pH value of 9.1 at the temperature of 25 ℃ together with NaCl of a concentration of 14 wt.% realized nearly 100% aniline recovery at the fifth stage of wastewater treatment. **Conclusions** High pH values and volume ratios of nitrobenzene/wastewater are more suitable for recovery of aniline. In addition, recovery of aniline is significantly elevated with increase of the concentration of salts, whose promoting effects are in the following order: $NaCl>Na_2SO_4>K_2SO_4>CaCl_2>KCl$ on the weight basis of wastewater. Furthermore, aniline in wastewater can be almost completely recovered by five-stage sequential nitrobenzene extraction, which is promoted continuously by the salting-out effect.

Key words: Aniline; Nitrobenzene; Extraction; Salting-out

INTRODUCTION

Aniline is an aromatic amine used as an intermediate in the manufacture of many dyes, pesticides and pharmaceuticals, and as chemical feedstock for rubber making. It is known to be a toxic water pollutant and its presence in wastewater even of a very low concentration has been shown to be harmful to aquatic life. In the United States, 62 facilities have reported to use or produce aniline. It is a hazardous substance that readily dissolves in water up to 3.5%. Thus, aniline solubility in water increases its risk of possible pollution not only to wastewater but also to drinking water sources in case of a chemical spill. During the period of 1981-1983, the National Institute for Occupational Safety and Health estimated that over 35 000 workers were potentially exposed to aniline[1]. Aniline has produced tumors in animals and increased the risk of bladder cancer in humans. OSHA regulates the permissible exposure limit for aniline at 2 ppm on an 8 h time weighted average (TWA) for skin absorption. In addition, the American Conference of Governmental Industrial Hygienists has put a threshold limit value (TLV) for aniline at 2 ppm on the 8 h TWA with a skin notation. The aquatic toxicity rating, TLm96, for aniline is 10 ppm, a concentration that will kill 50% of the exposed organisms within 96 hours[2].

Although aniline in water is subjected to bio and photo degradation, it is a toxic substance to aquatic life and must be eliminated from wastewaters before being released in natural watercourses. Several attempts have been made either to treat such types of effluents for facilitating easy disposal, or to recover the chemicals and recycle the process water. Traditional methods of purification such as, distillation, liquid extraction and absorption can be used for removal of organic contaminants from wastewater; however, industries are looking for competitive alternative technologies which may overcome some of the inherent disadvantages of the traditional processes[3-8]. Further, these processes suffer from the disadvantages that they are not necessarily efficient in removing organic solutes at parts per million levels from dilute solutions. Due to

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aniline's high boiling point (183 ℃), and generally low concentration, usually about 1% or lower in wastewater, distillation columns and other heat intensive separations require a large amount of energy to vaporize the high boiling material. Although traditional solvent extraction and activated carbon adsorption are the most commonly used processes for this purpose, application of these processes is sometimes restricted because of environmental or technical constraints. The traditional solvent extraction usually produces secondary liquid organic waste which may cause environmental problems, and activated carbon desorption is very difficult to carry out because of regeneration costs. Therefore, there is a need for development of a new extraction process through which aniline can be removed satisfactorily.

In this study, the multiple-stage extraction was applied to the removal of aniline from aqueous solution, because of easy operation, low operating costs, and fast handling speed at low temperature without destroying material. During the extraction, nitrobenzene was chosen as the solvent due to its common industrial use and recycled through the nitrobenzene hydrogenation process. The author investigated the role of inorganic salts, referred to as salting-out agents, in recovery of aniline from wastewater by means of solvent extraction. The effects of concentrations and different types of inorganic salts, acidity of wastewater, volume ratios of solvent to wastewater and extraction stages on the recovery percentage of aniline were elucidated simultaneously.

MATERIALS AND METHODS

Material and Apparatus

Nitrobenzene and aniline were procured from Shanghai Chemical Reagent Company (China), and $NaHCO_3$, NaCl, CaCl, K_2SO_4, Na_2SO_4, and KCl were obtained from Tianjin Chemical Company (China). Distilled water was used throughout the whole experiment. All reagents used in the present study were of the analytical grade. In preparation of aniline waste water, industrial wastewater composition was considered.

A thermostatic water bath vibrator was used for full inclusion of wastewater and extraction solvent.

Extraction

The experiments were performed in a homostatic water bath under common atmospheric pressure. Prior to testing, aniline wastewater with different concentrations was prepared. The extractor is pear-shaped separating funnel (250 mL). At the beginning of extraction tests, the operating variables, such as extracting temperature and stirring rate and so on, were adjusted to the set points. After extraction tests with an agitation time of 25 min, the extract decanted from the extractor was analyzed by a 721-spectrophotometer.

To elucidate the influence of concentrations of inorganic salts on extracting behaviors, four tests with various concentrations of each salt (0-14 wt.%) were carried out, wherein concentrations of salts were based on the weight of wastewater. The effects of acidity of wastewater (pH 3.2-10.8) and initial aniline concentration (1-5 wt%) on the extracting performance were also explored. Additionally, a series of tests with various volume ratios of solvent to wastewater (from 5% up to 30%) were performed. Furthermore, the multiple-stage extraction in presence of NaCl was undertaken successively to assess the feasibility of applying nitrobenzene extraction to treatment of wastewater. In this study, the extraction experiments were conducted in triplicate to check the reliability of testing results.

Analyses

To find out the aniline content dissolved in the raffinate, the wastewater raffinate was analyzed by a 721-spectrophotometer at a wavelength of 585 nm. Before analyses, the raffinate was diluted to 1:5.

Adjustment of pH Values of Wastewater

$NaHCO_3$ was specified as the acidity reagent. The pH value of the wastewater was increased gradually from 3.2, 5.2, 7.1, and 9.1 to 10.8 (detected by accurate pH test paper).

RESULTS

The effects of different factors on the extent of extraction of aniline have been discussed in the paper. The extent of extraction is defined as recover of aniline (%)=$(c_0\text{-}c)/c_0$, where c_0 is the concentration of aniline in the stock solution, c is the concentration of aniline in the water phase.

Effects of Acidity and Initial Concentration of Wastewater

For the sake of enhancing recovery of aniline from wastewater, the acidity of wastewater was adjusted by addition of $NaHCO_3$ alkaline solution with different initial concentrations. In this study, aniline recovery at five pH values, 3.2, 5.2, 7.1, 9.1, and 10.8 were investigated. These pH values stand for acidic, neutral and alkaline conditions

respectively. Fig. 1 shows the variation of recovery of aniline with the increase of the pH value and initial aniline concentration of the aqueous phase in solvent extraction. As shown in Fig. 1, the recovery of aniline increased with the rise of pH values.

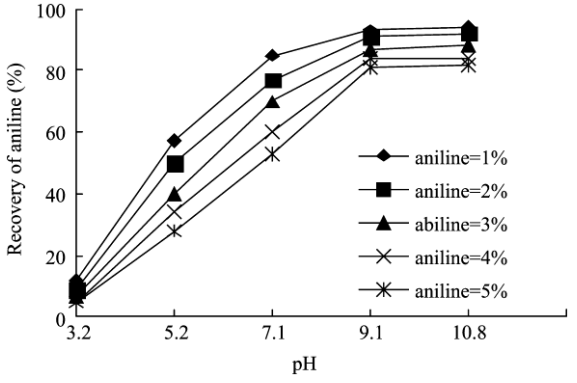

FIG. 1. Effect of pH value on recovery of aniline. (nitrobenzene/wastewater=5%, emperature =25 ℃).

Effects of Volume Ratios of Solvent to Wastewater

It has been well known that the adjustment of solvent amounts used is an important operating variable industrially. For successful recovery of aniline, it is desirable to use a minimum amount of nitrobenzene for maximum extraction of aniline. Fig. 2 shows the effect of concentration of nitrobenzene on extraction of aniline of different initial concentrations at 25 ℃. It has been observed that when the nitrobenzene concentration is lower than 20% (v/v), extraction of aniline increases sharply. When the aniline concentration exceeds 20%, the extraction of aniline remains practically constant, and from an economic point of view, nitrobenzene/wastewater (20%) was beneficially chosen for all subsequent experiments, thus leading to our adoption of a concentration of 20% of nitrobenzene in all later studies.

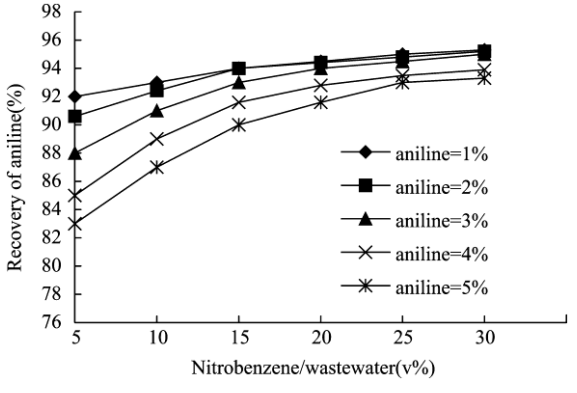

FIG. 2. Effect of volume ratios of solvent to wastewater on the recovery of aniline. (pH=9.1, temperature =25 ℃).

Effect of Concentrations and Different Types of Salts

The impact of different types of salt on aniline recovery was studied firstly, and then the influence of each salt of different concentrations on the recovery was considered. Fig. 3 illustrates the recovery percentage of aniline by nitrobenzene extraction in the use of different kinds of salts, such as NaCl, KCl, Na_2SO_4, K_2SO_4, and $MgSO_4$. Obviously, under the influence of NaCl, the maximum recovery of aniline was achieved. It clearly indicates that the amounts of organic compounds extracted exhibited an increasing trend with increase of concentrations of salts, including NaCl, KCl, $CaCl_2$, Na_2SO_4, and K_2SO_4.

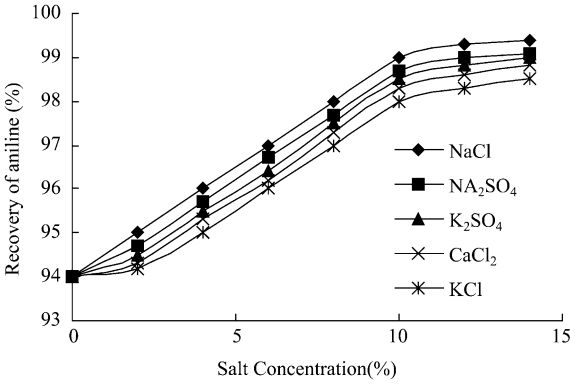

FIG. 3. Effect of different types of salts on the recovery of aniline. (nitrobenzene/waste water=20%, pH=9.1, temperature=25 ℃).

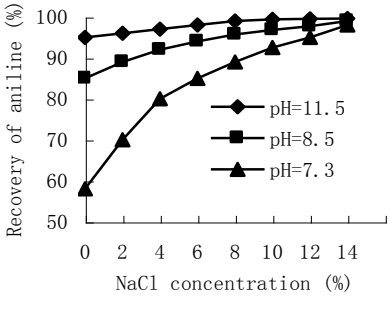

FIG. 4. Effect of NaCl concentration at various pH conditions. (nitrobenzene/wastewater=20%, temperature=25 ℃).

Effects of acidity of wastewater on the recovery percentage of aniline and salting-out results are demonstrated in Fig. 4. Obviously, without addition of inorganic salts, the extracting efficiency of aniline from wastewater with higher pH values was better than that with lower pH values. It can be attributed to different solubility of aniline in wastewater, which increased with the growth of the pH value[12-13]. As far as the addition of NaCl was concerned, the amount of aniline extracted was significantly

increased with increase of the concentration of NaCl at a range of pH7.3-11.5, similar to the trend mentioned in the previous paragraph.

Effect of Extraction Stages

For the purpose of increasing the recovery percentage of organic solutes, the multiple-stage extraction has always been adopted practically. Fig. 5 illustrates the influence of multiple-stage operation on the extracting behavior of nitrobenzene. The recovery percentage of aniline from wastewater was gradually increased with advance of the extraction stages either in the presence or in the absence of NaCl. Due to the existence of NaCl in wastewater, recovery of organic compounds was continuously promoted by salting-out effect in sequential extraction tests. As a consequence, the recovery percentage of aniline from wastewater accompanied with 6 wt.% of NaCl was significantly higher than that without NaCl. It is noteworthy that the value of recovery percentage reached a level as high as 99.6% at the fifth stage of wastewater treatment. Nonetheless, the amount of organic compounds extracted in the absence of NaCl only reached 96% at the fifth stage, and later extraction stages would not elevate the recovery of aniline. The later phenomenon observed might be interpreted by the dissolution of nitrobenzene solvent into wastewater, caused by longer contact time[14-15]. On the contrary, the solubility of nitrobenzene in aqueous phase has significantly diminished in the presence of NaCl, suggesting that nitrobenzene solvent was scarcely dissolved into wastewater, corresponding to our result, wherein there was no nitrobenzene detected. Therefore, the aniline in wastewater could be completely recovered by means of nitrobenzene extraction with the aid of salting-out effect[16].

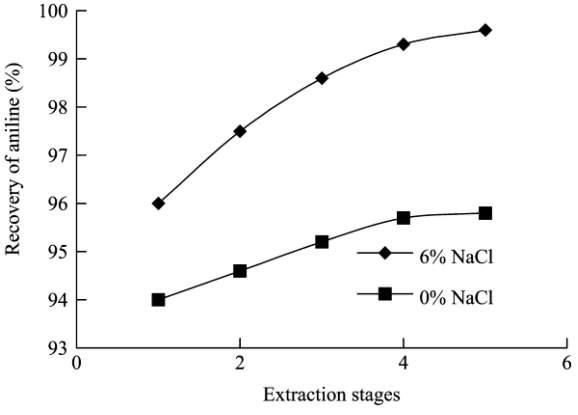

FIG. 5. Effect of the extraction stages on the recovery of aniline (nitrobenzene/wastewater=20%, pH=9.1, temperature =25 ℃).

DISCUSSION

Due to its dissociation in aqueous phase, aniline free molecules are most active in extremely alkaline media. This means that there would be more aniline free molecules available to be extracted into the organic phase. On the contrary, while in extremely acid media, there would be less aniline free molecules available to be transferred into the organic phase. The recovery of aniline was improved a little when the extraction pH value was higher than 9.1, suggesting that the pH value of 9.1 was the optimum pH value for the solvent extraction. It is obvious that pH values affected the recovery of aniline, but the initial aniline concentration also played an important role. As shown in Fig. 1, a change in pH values appeared to exhibit larger effect when the initial concentration of aniline decreased. By increasing the concentration of aniline, the importance of pH on the recovery of aniline decreased. For example, with the aniline concentration of 1%, the change in the recovery of aniline was about 83; however, when the aniline concentration was increased to 5%, the change in the recovery of aniline was decreased to about 70. As aniline solved in both phases, the composition changed with the increase of aniline concentrations. Then, the change of phase composition changed the activity coefficients of aniline. Therefore, the recovery of aniline, which depended on the activity coefficients, was affected by the change of the aniline concentration.

It has also been observed that at a particular nitrobenzene concentration, the percentage of extraction decreases with increase of initial aniline concentration. With increase of nitrobenzene concentration, the volume of the organic phase increases to maintain the material balance, as the concentration of nitrobenzene in the aqueous phase remains almost constant[9]. This increase of the volume of the organic phase renders a higher solubilization and adsorption of aniline, which explains the higher extraction percentage of aniline at higher nitrobenzene concentration at the constant temperature, pH value and initial aniline concentration.

This phenomenon may be interpreted with the salting-out effect, resulting from the existence of inorganic ions in wastewater, as suggested by several investigators[10-11], who have shown that the principal effect of inorganic salts upon organic solute solubility is the formation of hydrated shells around the ions, which effectively reduces the available amount of free water to dissolve organic solutes. Thus, it reveals that salts rank in the following order in terms of their salting-out effect which depends strongly upon both

the Setschenow constant and concentrations of inorganic salts: NaCl>Na_2SO_4>K_2SO_4>$CaCl_2$>KCl, on the weight basis of wastewater.

With regard to the increment of recovery percentage of aniline between 14 wt.% NaCl and 0 wt.% NaCl, as a function of pH values, it is apparent that the increment of recovery percentage at lower pH values is larger than that at higher pH values (i.e. Δ aniline pH 7.3 versus Δ aniline pH 11.5 = 40% : 4.6%). That suggests the salting-out effect depends strongly upon the acidity of wastewater. This phenomenon may be explained by higher solubility of aniline in the aqueous phase at pH 7.3, wherein the amount of free water is more than the amount of free water at higher pH values. As a result, the former is more seriously affected by salting-out effect, leading to decrease of the amount of free water.

CONCLUSION

Based on the above discussion, it is found that recovery of aniline is affected by acidity of wastewater, volume ratios of solvent to wastewater and inorganic salts. High pH values were more suitable for recovery of aniline. Further, the ration of nitrobenzene/wastewater 20% is conducive to recovery of aniline from wastewater. The recovery of aniline from wastewater was significantly enhanced by addition of inorganic salts, which rank in the following order in terms of their priority: NaCl >Na_2SO_4>K_2SO_4>$CaCl_2$>KCl on the weight basis of wastewater. That may be attributed to the salting-out effect, which depends strongly upon the acidity of wastewater. It is remarkable that aniline in wastewater would be completely recovered by five successive nitrobenzene extraction stages in the presence of NaCl.

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