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REGENERATION OF IONIC LIQUIDS DURING THE PRECIPITATION OF 2-NAPHTHALENESULFONIC ACID FROM AQUEOUS SOLUTION

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Introduction

Wastewater produced by dye production processes are contaminated by a large amounts of organic substances (high content of Chemical Oxygen Demand, COD). The main treatment problem of this wastewater is its low biodegradadability (expressed as ratio of Biological Oxygen Demand, BOD and COD).

2-Naphthalenesulfonic acid (Fig.1) is important intermediate in production of textile dyes. The major demand of 2-naphthalenesulfonic acid is production of β-salt (sodium 2-naphthalenesulfonate) for production of β-naphtol. β-Naphtol is used for production of solvent dyes, e.g. Solvent Yellow 14, in acid dyes, e.g. Acid Orange 7, in metalizable dyes, e.g. Mordant Black 15, and in pigments, e.g. Pigment Red 3 [1].

The 2-naphthalenesulfonic acid is the intermediate in the production of the 1,6-; 2,6-, and 2,7-disulfonic acids and the 1,3,6-trisulfonic acid. Nitration of 2-naphthalenesulfonic acid gives primarily the 5- and 8-nitro derivatives as intermediates for Cleve's acids [2].

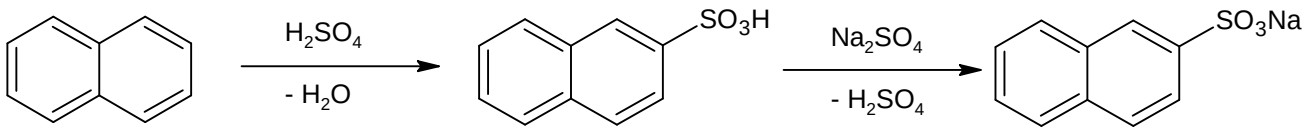

Figure 1 - Synthesis of 2-naphthalenesulfonic acid

Various special techniques are suitable for the removal of dyes from wastewater. These include coagulation, sorption on charcoal [3], chemical oxidation [4], or application of ionic liquids [5].

These mentioned wastewater treatment methods work satisfactorily at optimal conditions, e.g. appropriate temperature, pH, reaction time.

This work describes the best available techniques for the treatment of wastewater containing 2-naphthalenesulfonic acid by using ionic liquids (Fig.2). This method is based on ion exchange and subsequent formation of ion pairs.

Ionic liquids are quarternary ammonium or fosfonium salts with bulky organic cation and small inorganic anion. The ion pair produced by interaction of naphtalenesulfonic acid with appropriate ionic liquid containing bulk non-polar cation forms non-polar, in water insoluble matter.

For the removal of 2-naphthalenesulfonic acid from wastewater commercially available ionic liquid benzalkonium chloride (BAC) was successfully tested.

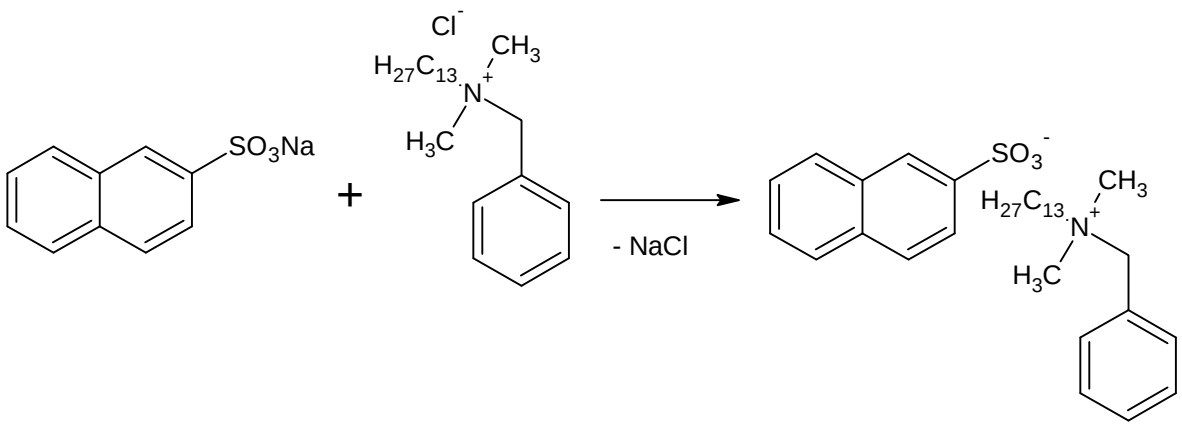

Figure 2 - Formation of ion pair (2-naphthalenesulfonic acid - Benzalkonium chloride)

The ionic liquid is potentially recyclable from ithe mentioned ion pair by desulfonation and subsequent evaporation of naphtalene. Recycled ionic liquid (benzalkonium sulfate) was reused repeatedly.

EXPERIMENTAL

Alkyldimethylbenzylammonium chloride (Benzalkonium chloride) was purchased from Sigma-Aldrich (USA), Sulphuric acid (96 mass %), sodium hydroxide (p.a.), sodium bicarbonate were supplied by Lach-Ner (Czech Republic). Naphthalene was supplied by DEZA (Czech Republic).

Synthesis of 2-naphthalenesulfonic acid:

100 g (0.78 mol) of naphthalene was heated to 100 °C in round bottom flask and 94.4 mL of sulfuric acid (96 wt.%, d = 1.84) was added. The reaction mixture was heated at 165°C for 5 minutes. After cooling, the mixture was poured into 750 mL of water, heated to boiling, and the charcoal was added. The reaction mixture was heated at 95°C for 1 hour. The reaction mixture was

filtered and $NaHCO_3$ was added until an alkaline reaction was obtained. The mixture was filtered, heated at 90°C and precipitated by Na_2SO_4. After standing overnight the sodium salt of the 2-naphthalenesulfonic acid was filtered (Filtrate: COD = 105 g · L^{-1})

The yield of 2-naphthalenesulfonic acid sodium salt was 127 g, which is 70.72 % of the theoretical yield.

Analyses of the chemical oxygen demand (COD) were carried out in accordance with the standard ČSN ISO 6060 (Czech Standards Institute, 1989) and the experimental error was less than 10 %.

Precipitation of 2-naphthalenesulfonic acid from aqueous solution:

75 mL of filtrate (contains 2-naphthalenesulfonic acid according to the calculation of input and output reaction streams) was poured into the beaker, and 14 mM solution of benzalkonium chloride was added and vigorously magnetically stirred using a magnetic stirrer Heidolph MR 3020 for 180 min. After precipitation the solution was filtered and parameter COD was measured in obtained filtrate (COD = 35 g · L^{-1}).

Regeneration of benzalkonium chloride:

The experiment was carried out in a 250-mL round bottom flask equipped with a stirrer, thermometer, and a water Liebig condenser.

The obtained ion pair (4.5 g) was transfered to the flask and 200 mL of sulfuric acid (63 wt. %) was added. The reaction mixture was heated at 130°C for 6 hours. Fumes of naphthalene was sublimated into the condenser during hydrolysis. In addition, during hydrolysis separation of the organic layer occurs. After cooling, the separated organic layer was collected and analyzed. It contains recycled benzalkonium sulfate and low quantity of sulfuric acid. Recycled benzalkonium sulfate were used for subsequent precipitation of 2-naphthalenesulfonic acid from diluted reaction mixture after separation of crude sodium salt of naftalenesulfonic acid.

CONCLUSION

In the first step, 2-naphthalenesulfonic acid was synthesized and the efficiency of the isolation process was found around 70 %. Diluted sulfuric acid saturated with organic residues (waste water) obtained as filtrate was neutralized and treated with commercialy available ionic liquid – benzalkonium chloride (BAC). This method was satisfactorily tested for the removal of dissolved 2-naphthalenesulfonic acid from aqueous filtrates obtained by isolation of 2-naphthalenesulfonic acid sodium salt. The removal efficiency of 2-naphthalenesulfonic acid using BAC was 85 % over 3 h (calculated according to the COD measurements).

In the next step, the ionic liquid and naphtalene were recycled by hydrolysis. The recycled benzalkonium sulfate was farther reused for treatment of filtrates obtained from next sulfonation step.

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