

UTILIZATION OF ACTIVATED CARBON IN COMBINATION WITH IONIC LIQUIDS FOR REMOVAL OF HALOGENATED DYES GROWING PARAMETER AOX FROM MODEL WASTE WATER

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Abstract

This work deals with the removal of chlorinated acid dyes such as Mordant Blue 9 and Acid Yellow 17 from model wastewater using granular activated carbon and ionic liquids. In this work, comparison of granular charcoal adsorption efficiency with subsequent effect of added aqueous mixture of benzylalkyldimethylammonium chloride (benzalkonium chloride) with methyltrialkylammonium chloride (Aliquat 336) on mentioned dyes removal efficiencies was studied. It was observed that addition of ionic liquid to the saturated active carbon enables enhancement of sorption capacity of this adsorbent.

Introduction

The water is most frequently used green solvent applicable for example for the production of anionic (or acid) azo dyes. Sulfonic acid groups bonded in the structures of anionic dyes make these colorants water soluble. The main method applied for the isolation of acid dyes from the aqueous reaction mixture is the precipitation of produced dye by salting out by addition of excess of sodium chloride and subsequent filtration. Obtained aqueous filtrate is in fact saturated aqueous solution of appropriate dye. Occurrences of chlorinated acid dyes in aqueous effluents increase chemical oxygen demand (COD) parameter and content of adsorbable organically bound halogens (AOX), in addition, there are non-biodegradable. The increasing cost of wastewater treatment requires needs for cheap and effective treatment techniques. Adsorption processes are being widely used for removal of dyes from waste water streams (1), however, these processes are limited by several factors like pH, salinity, quantity of contaminants, etc.

We proved that another method for effective removal of acid dyes from aqueous solution is based on ion exchange reaction caused by addition of hydrophobic quaternary ammonium or phosphonium halogenides (ionic liquids, $R_4N^+Cl^-$ or $R_4P^+Cl^-$) into the aqueous solution of acid dye (2-5). Ionic liquids (ILs) are low melting organic salts composed by large asymmetric organic cations and inorganic or organic anions. ILs exhibit very low vapour pressure under ambient conditions and thus are effectively non-volatile compounds. Some ionic liquids are water soluble, whereas the others are lipophilic and sparingly soluble (6).

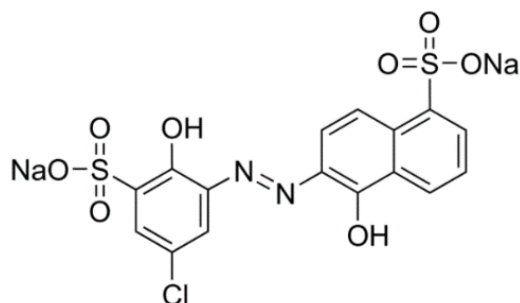


Figure 1. Chemical structure of Mordant Blue 9 (CAS Number: 3624-68-8)

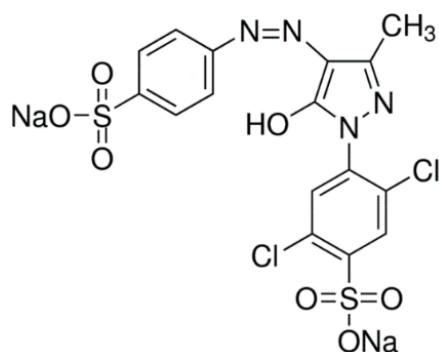


Figure 2. Chemical structure of Acid Yellow 17 (CAS Number: 6359-98-4)

Experimental part

Mordant Blue 9 and Acid Yellow 17 dyes and ionic liquids benzalkonium chloride and Aliquat 336 were supplied by Sigma-Aldrich Co. Granulated active carbon Hydrarffin CC 8X30 was obtained from Donauchem Co., Austria. A stock solution of dye (0.01mol/L) was prepared by dissolving the appropriate amount corresponding to 10 mmol of Mordant Blue 9 or Acid Yellow 17 dyes in 100mL and completing to 1000 mL with distilled water. The separation efficiencies of dyes removal were analysed using UV-VIS spectroscopy. The removal efficiency (*RE* %) of dyes was determined from absorbance measurements according to the concentration absorbance standard curves at the respective maximum adsorption wavelength of the individual dye solutions (see Table 1). The prepared dye solutions were diluted to the 1 mM concentration by tenfold dilution with demineralized water.

Afterwards, *RE* % was calculated from Eq.1:

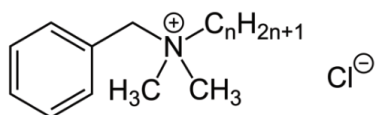
$$RE (\%) = (1 - A/A_0) \times 100 \quad (\text{Eq. 1})$$

,where *A* and *A*₀ denote the absorbance in the solution after and before precipitation, respectively.

The laboratory glass adsorption column was filled using granular activated carbon (50 grams). Activated carbon was first rinsed with water to wash out the coal dust. Subsequently, the adsorbent was saturated using 1 mM aqueous dye solution using flow rate 150 mL per hour till absorption of effluent at absorption maximum reached *A* value of used 1 mM dye solution. The amount of dye was dosed in 200 mL of 1 mM solution for each wash, the wash time was 70-90 minutes. Determination of charcoal removal efficiency (amount of dye removed from the model aqueous dyes solutions) was determined according to the Lambert-Beer law measuring absorbance *A* at absorption maximum of appropriate dye (see Table 1).

The saturation of the activated carbon adsorption layer was accomplished until absorbance of the eluate at *A*_{max} was greater than 18.34 for Mordant Blue 9 and 19.54 for Acid Yellow 17 (see Table 1).

In the next step, the saturated layer of adsorbent was impregnated with 2.5 g of aqueous ionic liquids mixture (benzalkonium chloride 50% : Aliquat 336 1: 1) and subsequently the impregnated layer of granulated active carbon was washed with 100 mL of demi water in the rate 70 mL per hour. The quantity of desorbed dye in obtained eluate was analysed on a spectrophotometer. The activated carbon thus prepared was further saturated with 1 mM dye solution at the flux rate 150 mL/h until saturation. Each 200 mL portion of obtained eluate was analysed on a spectrophotometer. After saturation of sorption layer, the closed sorption column was left overnight, and a next impregnation of sorption layer and subsequent removal of dye from 1 mM aqueous dye solution was studied according to the above described procedure. The impregnation of sorbent and subsequent separation of dye was performed 3-times in three days. The experiment was repeated three times in each experiment (see Figures 5 a 6).



$$n = 8, 10, 12, 14, 16, 18$$

Figure 3. Chemical structure of commercially available ionic liquid benzalkonium chloride

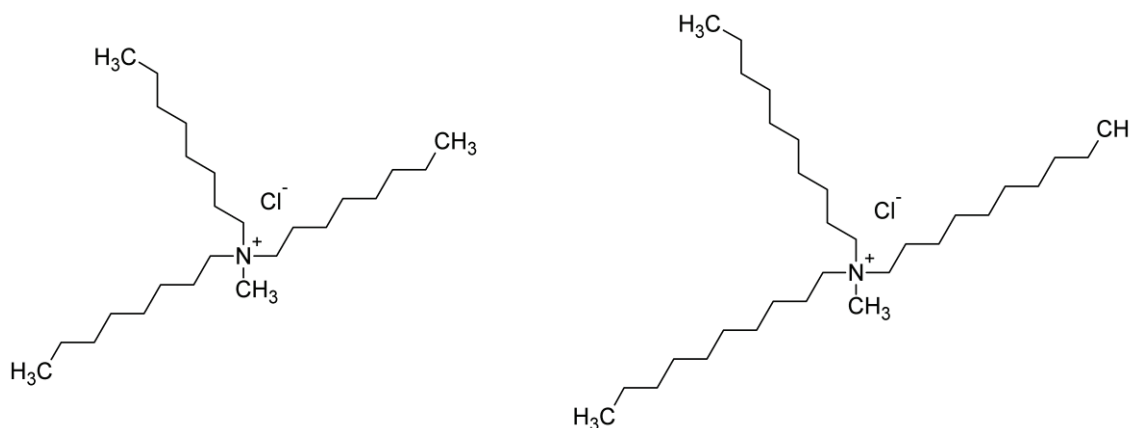


Figure 4. Chemical structure of commercially available ionic liquid Aliquat 336:

Table I: Specification of studied dyes

Used dye	c [molL ⁻¹]	Quantity of dye [g/L]	λ_{\max} [nm]	Measured absorbance of 10 mM dye solution at λ_{\max}
Mordant Blue 9	0.01	10.56	516	183.4
dye content 50 %				
$M_r=502.81$ g/mol				
Acid Yellow 17	0.01	11.23	400	195.4
dye content 50 %				
$M_r=551.29$ g/mol				

Results and discussion

Measured absorbances of all the analysed samples of eluates dealing with sorption efficiencies of acid dye Mordant Blue 9 are depicted in Figure 1. As could be seen, using approximately 2 liters of 1 mM solution of Mordant Blue 9 caused complete saturation of 50 g granulated active carbon layer used as the sorbent (see Figure 1). After subsequent addition of ionic liquids solution (impregnation of charcoal with mixture of ILs, the absorbance of subsequent eluent dropped from initial value of 14.31 to less than 8, however, quickly turned to 14 ± 4 . Similarly, testing sorption of Acid Yellow 17, the active carbon layer in adsorption column was saturated after elution of ca. 2 liters of 1 mM aqueous solution (see Figure 2). After subsequent addition of ionic liquids solution (impregnation of charcoal with mixture of ILs, the absorbance of subsequent eluent dropped from initial value of 14.31 to less than 8, however, quickly turned to 16 ± 4 . However, next addition of aqueous solution of ionic liquids caused increase of removal efficiency of impregnated sorbent layer.

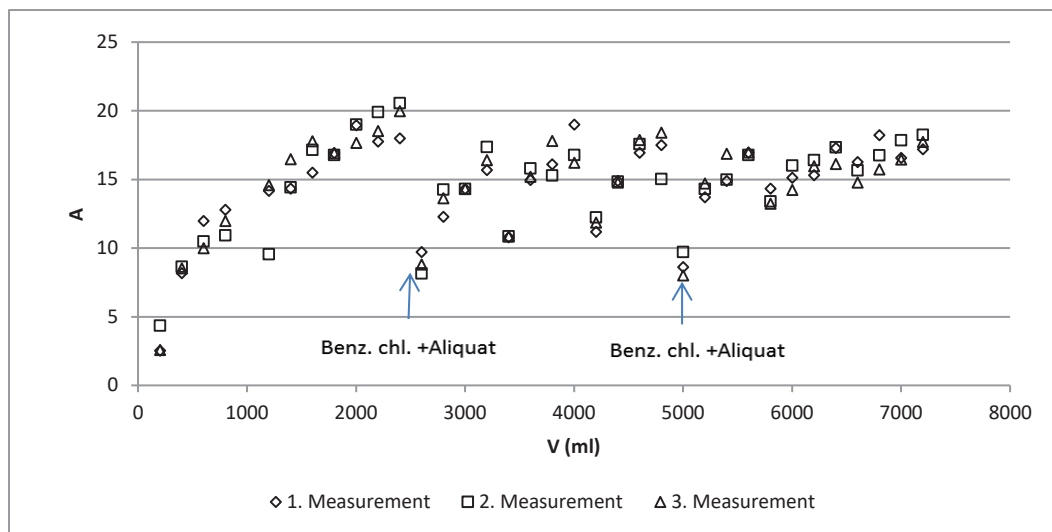


Figure 5. The amount of removed dye Mordant Blue 9

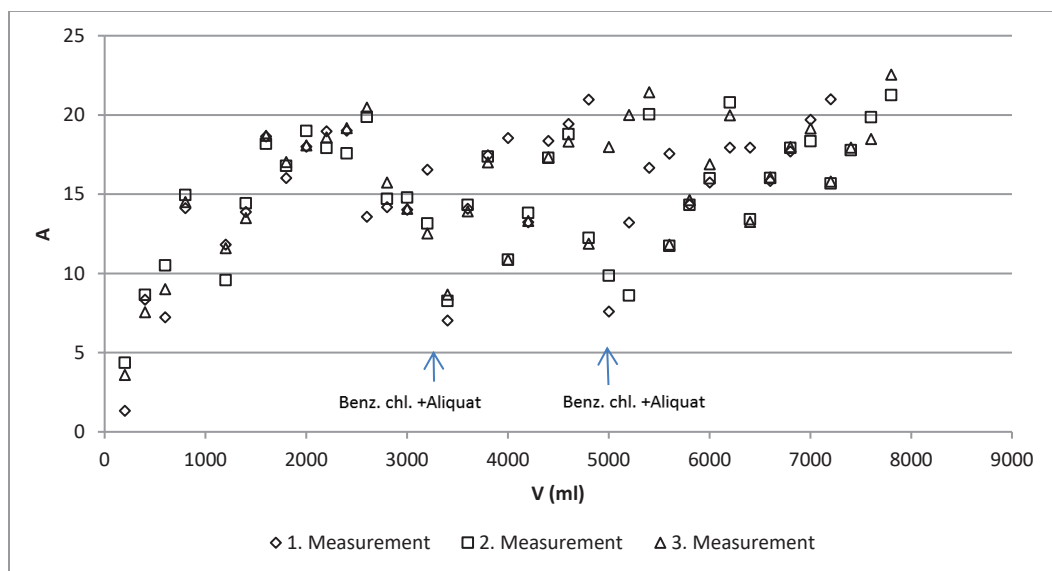


Figure 6. The amount of removed dye Acid Yellow 17

Conclusion

The paper deals with the use of activated carbon to remove halogenated acid dyes increasing the AOX parameter from model wastewater. Classic activated carbon was used to remove of two halogenated dyes from model wastewater. It was verified that at least part of sorption activity of saturated sorbent layer should be reactivated using addition of cheap ionic liquids (benzalkonium chloride, Aliquat 336) to the deactivated charcoal. Furthermore, this technique was repeated 3-times with similar results. Generally, application of ILs for separation of organic acids from aqueous solution is probably promising alternative method for cost-effective production of specialty organic chemicals.

Acknowledgement:

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