Application of weakly basic anion exchanger for removal of Remazol Black B

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The weakly basic anion exchangers of the functional tertiary amine gropus with the polystyrene skeleton: Amberlyst A-21 and with acrylic skeleton: Amberlite IRA-67 were investigated as adsorbents of Remazol Black B from aqueous solutions. Experiments were carried out as function of contact time (1–240 min.), initial dye concentration (50–500 mg/dm^3), pH (1–12), temperature (298–318 K) and ionic strength (NaCl). The results indicate that the investigated anion exhchangers are suitab;e as adsorbent material of Remazol Black B from aqueous solutions.

Keywords and phrases: Remazol Black B, anion exchanger, sorption.

Introduction

The scale and growth of the dyes industry has been inextricably linked to that of the textile industry. World textile production has grown steadily to an estimated 35×10^6 t in 1990. The two most important textile fibers are cotton, the largest, and polyester. Consequently, dye manufactures tend to concentrate their efforts on producing dyes for two fibers. The estimated world production of dyes in 1990 was 1×10^6 t [1]. Although most dyes are non-toxic at the concentration detected in wastewaters, the color is undesirable to the water user. Dyes are difficult to be removed, since they are recalcitrant organic molecules, resistant to aerobic digestion and is stable to light, heat and oxidizing agents [2]. Another difficulty is treatment of wastewaters containing low concentrations of dye molecules. In this case, common methods for removing dyes are either economically unfavorable and/or technically complicated. Because of high costs associated with the practical applications to remove trace amounts of impurities, many of methods of treating dyes in wastewater have not been widely applied on large scale in the textile industries [3]. It is now recognized that ion exchange is an effective method for the water decontamination. It is basically a reversible chemical process where the ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle [4]. Ion exchange has been fruitfully used for the removal of the dyes [5–7].

Materials and methods

Materials

Dye

Remazol Black B was chosen in this study because it is a dye widely used in textile industry of different commercial names such as Reactive Black 5, Cavalite Black B, Celmazol Black B, Diamira Black B, Drimarene Black R/K 3B, Intracron Black VS-B, Levafix Black E-B, Primazin Black BN, Remazol Black GF, Sumifix Black B. It is a black disazo reactive vinylosulfonyl dye used for urea- and sodium bicarbonate-padded cotton utilizing stream or dry heat for fixing [8].

The textile dye, Remazol Black B (C.I. number: 20505, molecular formula: $C_{26}H_{21}N_5Na_4O_{19}S_6$, molecular weight: 991.82 g/mol) was purchased from Sigma-Aldrich (Germany) and used without further purification (dye purity: 55%). RB5 [4-Amino-5--hydroxy-3,6-bis((4-((2-(sulfooxy)ethyl)sulfonyl)phenyl) azo)-2,7-naphthalenedisulfonic acid tetrasodium salt] is dissociated anionic sulfonate in aqueous solution with the molecular structure presented in Fig. 1. The dye is highly soluble with a solubility of > 50 g/L. Its molecule has a size of 3.15 × 1.23 × 0.92 nm [9].

The dye was used as supplied without purification, and the fraction of inert material was not taken into account in the calculation of dye concentration.

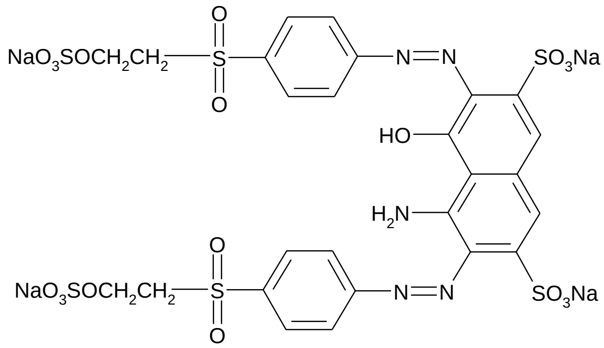

Fig. 1. Chemical structure of Remazol Black B.

Resins

The weakly basic resins Amberlyst A-21 and Amberlite IRA-67 were used for sorption studies. The anion exchangers were supplied by Rohm and Haas (France). Important physical and chemical properties of these resins are presented in Table 1.

The resins were washed with distilled water to remove impurities and dried.

Table 1. Anion exchanger characteristics.

Description	Amberlyst A-21	Amberlit IRA-67
Type	Weakly basic	
Functional groups	¾N(CH$_3$)$_2$	
Matrix	Styrene divinylo-benzene	Acrylic divinylo-benzene
Structure	Macroporous	Gel
Ionic form as shipped	Free base	
Bead size [mm]	0.49–0.69	0.50–0.75
Total capacity [eq/dm^3]	≥ 1.25	≥ 1.60
Max. operating temp. [°C]	100	60
Producer	Rohm and Haas, France	Rohm and Haas, France

Aparatus

A laboratory shaker (Elphine type, Poland) was used to shake the anion exchangers and liquid phases. An UV-VIS spectrophotometer (Specord M 42, Carl Zeiss Jena, Germany) was used for absorbance measurements of the samples. The maximum wavelength (λ_{max}) used for determination of residual concentration of Remazol Black B in the supernatant solution using a UV-VIS spectrophotometer.

Batch method

A known amount of dry resin (0.2 g) was shaken with 20 cm^3 solution of Remazol Black B from 1 to 240 minutes at 298–318 K. After the desired time, the resin was filtered and then the dye concentration was determined using the UV-VIS method. The data obtained from the adsorption tests were used to calculate the adsorption capacity, q_t (mg/dm^3) from the following equation:

$$q_t = \frac{(c_0 - c_t)}{w} \times V \qquad (1)$$

where: c_0 — the initial concentration of Reactive Black 5 in the aqueous phase;
c_t — the concentration of Reactive Black 5 in the solutions after time t;
V — the volume of the solutions (dm^3);
w — the weight of the dry anion-exchanger (g).

To determine the effect of initial concentrations of the dye on the adsorption rate , the initial concentration of the dye was varied between 50 and 500 mg/dm^3. The effect of initial pH of the dye solution was investigated in the pH range from 1 to 12 for the initial dye concentration of 200 mg/dm^3 at 298 K. The effect of temperature was studied for three different temperatures (298, 308, 318 K). NaCl were employed as background electrolyte change between 0 to 100 g/dm^3 to investigate the influence of ionic strength on the dye removal.

Results and discussion

It is observed that the extent of adsorption of Remazol Black B from solution at the initial dye concentration from 100 to 500 mg/dm^3 on the examined anion exchangers increases of time until it reaches equilibrium adsorption amount. The extent of adsorption is observed to increase rapidly during the adsorption starting step and then followed by a slowly increase in the following adsorption. The adsorption capacities at equilibrium increase from 9.99 to 49.93 mg/g for Amberlyst A-21 (Fig. 2) and from 9.97 to 49.97 mg/g for Amberlite IRA-67 (Fig. 3) at the initial dye concentration range with the anion exchanger dose of 10g/l. it is expected that the increase of adsorbate initial dye concentration in solution could produce a stronger driving force, which could result in more chances for dye molecular reaching the surface of the anion exchanger. As the result, the adsorption capacity increased with the increase of adsorbate initial dye concentration.

Sorption of Remazol Black B on Amberlyst A-21 is practically not influenced by the initial pH of an aqueous

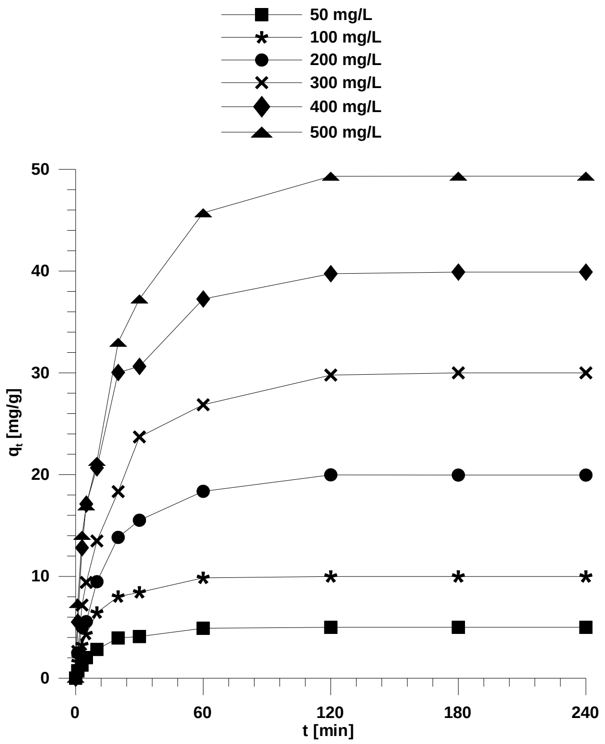

Fig. 2. The effect of phase contact time on sorption of Reactive Black 5 on Amberlyst A-21.

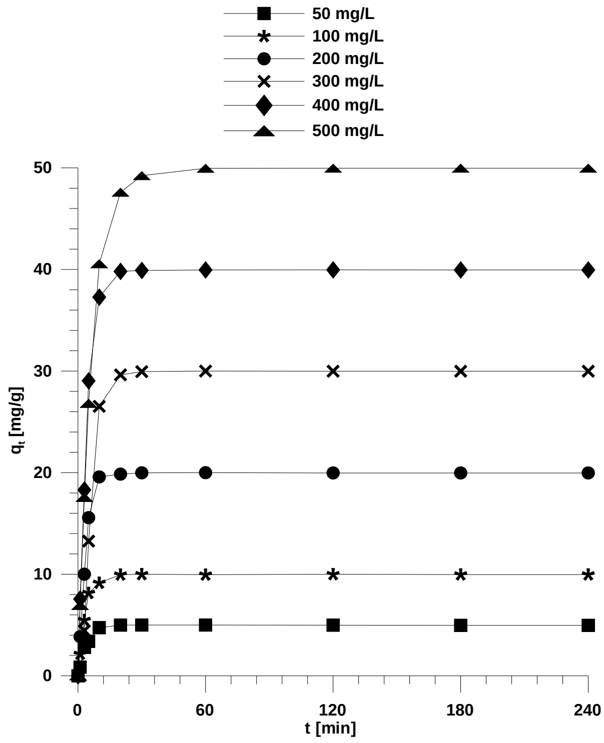

Fig. 3. The effect of phase contact time on sorption of Reactive Black 5 on Amberlite IRA-67.

medium at range from 1 to 12 (Fig. 4). In the case of Amberlite IRA-67 (Fig. 5), the decrease in the sorption capacity of the anion exchanger at the initial Remazol Black B pH < 9 may be attributed to the deprotonation of the tertiary amine groups. Furthemore, the sorption capacity of anion exchanger is significantly decreased because an excess of OH^- corresponding to a high pH resulted in the strong competition of anions, brought about by the base used for varying of pH.

Temperature is an important parameter for the adsorption process. The adsorption of Remazol Black B at higher temperatures was found to be greater than that at lower temperature in the case of both anion exchangers. The increase in temperature would increase the mobility of the large dye ions as well as produce a swelling effect with the internal structure of the examined anion exchangers, thus enabling the large dye molecules to penetrate further. Therefore, the adsorption capacity should largely depend on the chemical interaction between the functional groups on the adsorbent surface and the adsorbate, and should increase as the temperature rises. This can be explained by an increase in the diffusion rate of the adsorbate into the pores. At higher temperatures the adsorbent might contribute to the adsorption of Remazol Black 5, as diffusion is an endothermic process.

The ionic strength of the solution is one of the factors that control both electrostatic and non-electrostatic

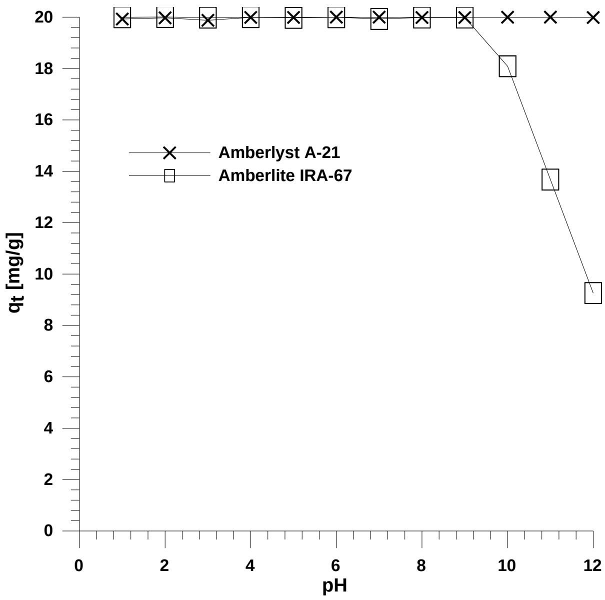

Fig. 4. The effect of initial pH on sorption of Reactive Black 5 on Amberlyst A-21 and Amberlite IRA-67.

interactions between the adsorbate and adsorbent surface. To determine whether the on-going adsorption process was affected by salt (ionic strength), Remazol Black B adsorption studies over weakly basic anion exchangers were carried out at sodium concentrations of 0 and 100 g/dm^3 with the constant initial dye concentrations of 200 mg/dm^3, adsorbent dose

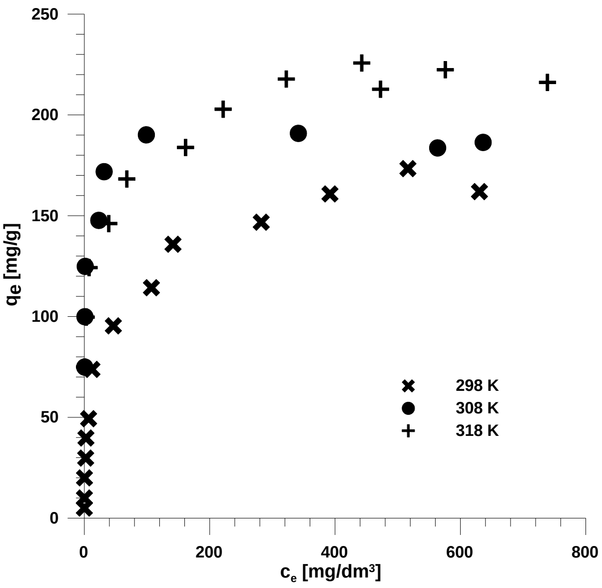

Fig. 5. The effect of temperature on sorption of Reactive Black 5 on Amberlyst A-21.

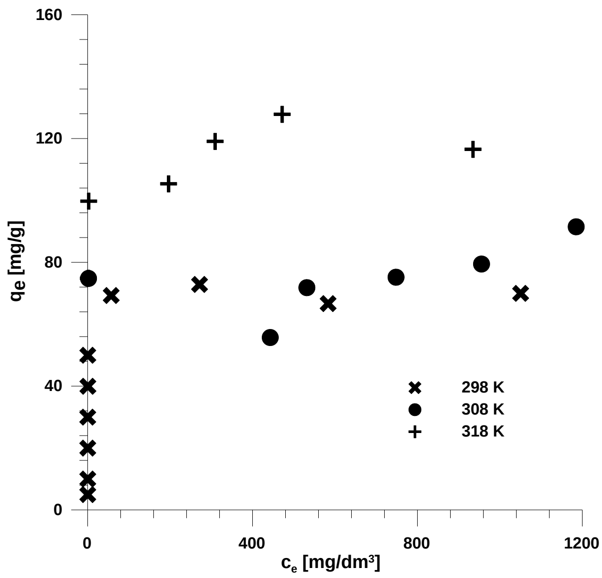

Fig. 6. The effect of temperature on sorption of Reactive Black 5 on Amberlite IRA-67.

10 g/dm³ and contact time of 3 h. The presence of NaCl produce a significant change of sorption capacity of Amberlyst A-21 for Remazol Black B. In the case of Amberlite IRA-67, NaCl has slightly negative effect on dye sorption, discernible above 10g/dm³. This indicates that Cl^- ions do not compete with sulfonate groups of the dye molecules for amine sites of weakly basic anion exchangers. Dyeing processes consume large amounts of salt. Therefore, the concentration of salt in dye wastewater can be normally high. Textile wastewaters can have a wide range of pH values and dyeing processes involve adding high concentrations of salts such as Na_2SO_4 and NaCl to enhance bath exhaustion, as well as carbonates to adjust pH. From this point of viev, this results indicates that the Amberlyst A-21 and Amberlite IRA-67 can be used for removal of Ramazol Black B from salt containing water.

Conclusion

The results obtained in this study indicate that the weakly basic anion exchangers: Amberlyst A-21 and Amberlite IRA-67 can be successfully used for the removal of hazardous dye, Remazol Black B, from aqueous solution.

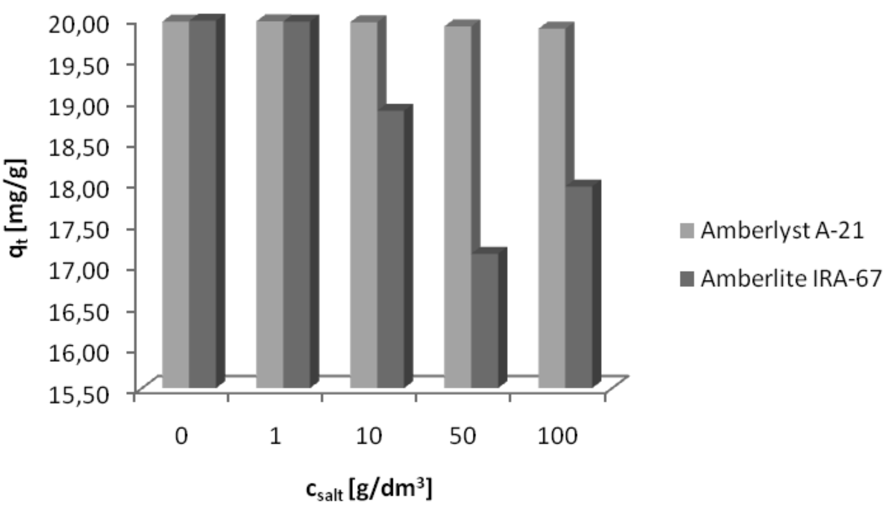

Fig. 7. The effect of ionic strength on sorption of Reactive Black 5 on Amberlyst A-21 and Amberlite IRA-67.

References

[1] Hunger, K. *Industrial Dyes, Chemistry, Properties, Applications.* Weinheim: Willey-VCH, 2003.

[2] Azlan, K., W.N. Wan Saime, and L. Lai Ken. "Chitosan and chemically modified chiosan beads for acid dyes sorption". *Journal of Environmental Sciences* 21 (2009): 296.

[3] Crini, G., and P.-M. Badot. "Application of chitosan, a natural aminopolysacharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature". *Progress in Polymer Science* 33 (2008): 399.

[4] Gupta, V.K., and Suhas. "Application of low-cost adsorbents for dye removal — A review". *Journal of Environmental Management* 90 (2009): 2313.

[5] Wawrzkiewicz, M., and Z. Hubicki. "Kinetic studies of dyes sorption from aqueous solutions anto the strongly basic anion-exchanger Lewatit MonoPlus M-600". *Chemical Engineering Journal* 150 (2009): 509.

[6] Karcher, S., A. Kornmüller, and M. Jekel. "Screening of commercial sorbents for the removal of reactive dyes". *Dyes and Pigments* 51 (2001): 111.

[7] Dulman, V., et al. "Adsorption of anionic textile dye Acid Green 9 from aqueous solution onto weak or strong base anion exchangers". *Journal of Applied Polymer Science* 113 (2009): 615.

[8] Gibbs, G., J.M. Tobin, and E. Guibal. "Influence of chitosan preprotonation on Reactive Black 5 sorption isotherms and kinetics". *Industrial and Engineering. Chemistry Research* 43 (2004): 1.

[9] Qiu, Y., and F. Ling. "Role of surface functionality in the adsorption of anionic dyes on modified polymeric sorbents". *Chemosphere* 64 (2006): 963–971.