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Application of weakly and strongly basic anion exchangers for the removal of brilliant yellow from aqueous solutions

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ABSTRACT

The weakly and strongly basic anion-exchangers (Amberlite IRA-67, Amberlite IRA-958, Amberlite IRA-402) of acrylic or styrene–divinylbenzene matrices have been applied for Brilliant Yellow (BY) removal from the aqueous solutions. The total ion exchange capacities (9.1×10^{-4} mol/g, 6.12×10^{-4} mol/g and 4.38×10^{-5} mol/g for Amberlite IRA-958, Amberlite IRA-67, Amberlite IRA-402, respectively) as well as recovery factors of Brilliant Yellow were determined by the batch method. The influence of phase contact time, pH and temperature was studied. The anion-exchangers modified by means of Brilliant Yellow were also applied in order to remove Cu(II), Ni(II) or Co(II) ions from chloride solutions. As follows from the results, the anion exchangers of acrylic-divinylbenzene matrix can be widely recommended for BY removal from waters and wastewaters originating from textile industry because of their high selectivity.

Keywords: Brilliant yellow; Azo dyes; Anion exchangers; Sorption; Removal; Wastewaters

1. Introduction

Azo dyes (including the sulphonated azo dyes) are a very important class of synthetic colours characterized by the presence of one or more chromophoric azo groups (–N=N–) in their structure [1–3]. Since the second half of the 19th century, they have been extensively used in numerous industrial branches. Currently, there are over 3000 azo dyes in use worldwide and they account for 65% of the commercial dye market [1].

Large quantities of sulphonated azo dyes are applied in many fields of up-to-date technologies, e.g. textile industry, paper production, leather tanning industry, food and cosmetics as well as in photoelectrochemical cells, photography and reprography, for pharmaceutical and medical diagnostic purposes and in agricultural research [4]. Moreover, synthetic dyes containing sulphonic groups have been employed as indicators for the determination of some metal ions because they are the most versatile chelating agents forming stable complexes with heavy metal ions [5,6]. A wide group of sulphonated azo dyes has also been immobilized on anion-exchange resins in order to transform them into chelating resins which can be used in sorption – spectroscopic test methods for sensitive determination of metal ions in the environmental analysis [7]. Promising results have been obtained using: SPADNS (2-(p-sulphophenylazo)-1,8-dihydroxy-3,6-naphtalenedisulfonate) [5], Pyrocatechol Violet [6,8], Eriochrome Black T [9] or Acid Orange 8 [10].

Due to large-scale production and extensive application, sulphonated azo dyes can cause considerable environmental pollution and are serious health-risk factors. However, the stringent regulations for the quality of potable water have led to enhanced interest in the decontamination of wastewater. A wide range of methods has been developed for the removal of synthetic dyes

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from waters and wastewaters to decrease their impact on the environment. The technologies involve adsorption on organic or inorganic matrices, decolorization by photocatalysis, and/or by oxidation processes, microbiological or enzymatic decomposition, etc. [4,11].

The paper is aimed at the studies on usefulness of the weakly and strongly basic (type I) anion-exchange resins: Amberlite IRA-67, Amberlite IRA-402 and Amberlite IRA-958 in recovery of the sulphonated azo dye — Brilliant Yellow (BY) from aqueous solutions. The batch experiments were carried out in order to determine the recovery factors of Brillant Yellow (%*R*). The effect of initial concentration of Brilliant Yellow and phase contact time on the percentage uptake was investigated. The influence of temperature and pH on adsorption of the dye on the above mentioned anion-exchangers was studied. The adsorption isotherms of Brilliant Yellow on Amberlite IRA-67, Amberlite IRA-402 and Amberlite IRA-958 were determined, too. The breakthrough capacities of Brilliant Yellow for the anion-exchangers were calculated from the breakthrough curves.

The anion exchange resins modified by means of 2,2'(1,2-ethenediyl)bis[5-[(4-hydroxyphenyl)azo] benzenesulfonic acid]disodium salt (Brilliant Yellow) were also applied in order to remove Cu(II), Ni(II) or Co(II) ions from aqueous chloride solutions.

2. Material and methods

2.1. Materials

2,2’(1,2-ethenediyl)bis[5-[(4-hydroxyphenyl)azo] benzenesulfonic acid]disodium salt known as Brilliant Yellow (Fig. 1) was produced by POCh (Poland).

Three anion-exchangers — the weakly basic (Amberlite IRA-67) and the strongly basic (Amberlite IRA-402 and Amberlite IRA-958) were supplied by Rohm & Haas (France). Their characteristics are compiled in Table 1.

Salts of Cu(II), Ni(II), Co(II) as well as HCl and NaOH were of analytical quality (POCh, Poland). Deionized water was used for preparation and dilution of all solutions.

2.2. Recovery factors

The samples of dry resin (0.2 g) were shaken mechanically with 20 cm^3 of corresponding azo dye solutions (1×10^{-4}–1×10^{-2} M) from 1 to 240 min at different temperatures (20–60°C). Afterwards, the anion exchanger was filtered off in order to determine the content of BY uptake.

The Brilliant Yellow recovery factors (%*R*) were calculated from Eq. (1):

$$\%R = \frac{C_a}{C_o} \times 100\% \qquad (1)$$

where C_a is the amount of dye adsorbed in the anion-exchanger phase and C_0 is the initial concentration of BY.

From these experiments, %*R* of Brilliant Yellow depending on time, pH of the solution, initial dye concentration as well as on temperature were obtained.

2.3. Adsorption equilibrium

Adsorption equilibrium of BY on the anion exchangers was investigated by batch method. Twenty milliters of the dye solution of different initial concentrations were shaken with 0.2 g of the dry anion exchanger in a

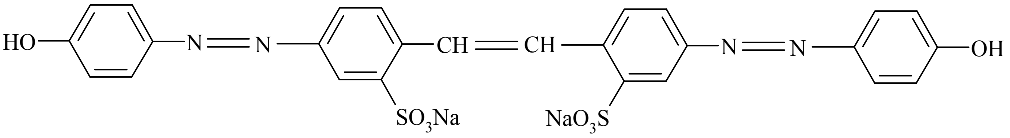

Fig. 1. Brilliant Yellow structure.

Table 1
Physicochemical properties of the anion-exchangers

Description	Amberlite IRA-67	Amberlite IRA-402	Amberlite IRA-958
Type	Weakly basic	Strongly basic	Strongly basic
Functional groups	$-N(R)_2$	$-N^+(CH_3)_3$	$-N^+(CH_3)_3$
Matrix	Acrylic divinylbenzene	Styrene divinylbenzene	Acrylic divinylbenzene
Structure	Gel	Gel	Macroreticular
Ionic form as shipped	Free base	Cl^-	Cl^-
Bead size, mm	0.50–0.75	0.60–0.75	0.63–0.85
Total capacity, eq/dm^3	≥1.6	≥1.3	≥0.8
Max. operating temperature, °C	60	60	80
Producer	Rohm & Haas	Rohm & Haas	Rohm & Haas

thermostated shaker (Elpin 358S) for 120 min at 25°C in the 100 ml Pyrex conical flask. After specific time the contents of the flask were filtered off and the concentration of BY was determined using the UV-VIS spectrophotometer (Specord M42). The data obtained from the adsorption tests were used to calculate the adsorption capacity, Q (mol/g) from Eq. (2):

$$Q=\frac{\left(C_o-C_t\right)}{w}\times V \qquad (2)$$

where C_o and C_t are the concentrations of the dye in the solution before and after sorption, respectively (mol/dm^3), V is the volume of the solution (dm^3) and w is the weight of the dry adsorbent (g).

2.4. Modification procedure

0.2 g of the anion exchanger were shaken with 20 cm^3 of Brilliant Yellow solution of 1×10^{-4} M concentration. After 2 h of mixing the equilibrium was reached. Then the resin was filtered off and thoroughly rinsed with distilled water. It was dried at room temperature. Affinity of the modified anion exchangers towards Cu(II), Ni(II) or Co(II) ions was evaluated by shaking the dry modified resin (0.2 g) with 20 cm^3 of the corresponding chloride metal solutions (63.55 µg Cu(II)/cm^3 or 58.55µg Ni(II)/cm^3 or 59.55 µg Co(II)/cm^3). The recovery factors of Cu(II), Ni(II) or Co(II) depending on the phase contact time (from 1 to 240 min) on the modified anion exchanger were calculated from Eq. (1) by analogy. The remaining metal ion concentration in the aqueous phase was determined by Perkin-Elmer 403 AAS.

2.5. Breakthrough capacities

The dynamic procedures were applied. The one-centimetre diameter columns were filled with swollen anion exchangers in the amount of 10 cm^3. Then BY solutions of the 1×10^{-4} M initial concentration were passed through the anion exchanger bed at the rate of 0.35 cm/min. The eluate was collected in the fractions and the dye content was determined. The working ion exchange capacities (C_r) were calculated from the breakthrough curves and are expressed in g of dye per dm^3 of the swollen anion exchanger.

All collected values in this paper are the average of three independent experiments.

3. Results and discussion

3.1. Adsorption of Brilliant Yellow

Brilliant Yellow exhibits a high affinity not only for the strongly basic Amberlite IRA-958 but also for the weakly basic Amberlite IRA-67 anion exchanger. The sorption mechanism of this azo dye ($R'(\mathrm{SO_3})_2{}^{2-}$) on a strongly basic anion exchanger in the chloride form (RCl) can be described by means of the reaction:

$$2R\mathrm{Cl}+R'(\mathrm{SO_3})_2^{2-}\rightarrow R_2(\mathrm{SO_3})_2R'+2\mathrm{Cl}^-$$

As follows from the above, Brilliant Yellow ($R'(\mathrm{SO_3})_2^{2-}$) forms a stable ion pair in the anion exchanger phase, but the surface interactions with the aromatic ring must be also taken into account.

It was found that affinity of this azo dye for the anion-exchangers depends on the composition (acrylic-divinylbenzene or styrene-divinylbenzene) as well as structure (gel or macroreticular) of the anion-exchanger matrices and can be presented in the following series: Amberlite IRA-958 > Amberlite IRA-67 > Amberlite IRA-402.

The total ion exchange capacities for Brilliant Yellow are equal to 9.1×10^{-4} mol/g, 6.12×10^{-4} mol/g and 4.38×10^{-5} mol/g for Amberlite IRA-958, Amberlite IRA-67, Amberlite IRA-402, respectively (Fig. 2).

On the laboratory scale there are most frequently determined total ion exchange capacity because working capacity is a changing value, different for various working conditions. On the industrial scale total exchange capacity is of less importance. However, working capacities is of significant importance as it is exploited in the ion-exchanger work. Therefore working capacities of the anion-exchangers in question were determined from the breakthrough curves.

They equal 1.77×10^{-2} mol/dm^3, 2.2×10^{-2} mol/dm^3 and 1.97×10^{-1} mol/dm^3 for Amberlite IRA-402, Amberlite IRA-67 and Amberlite IRA-958, respectively (Fig. 3).

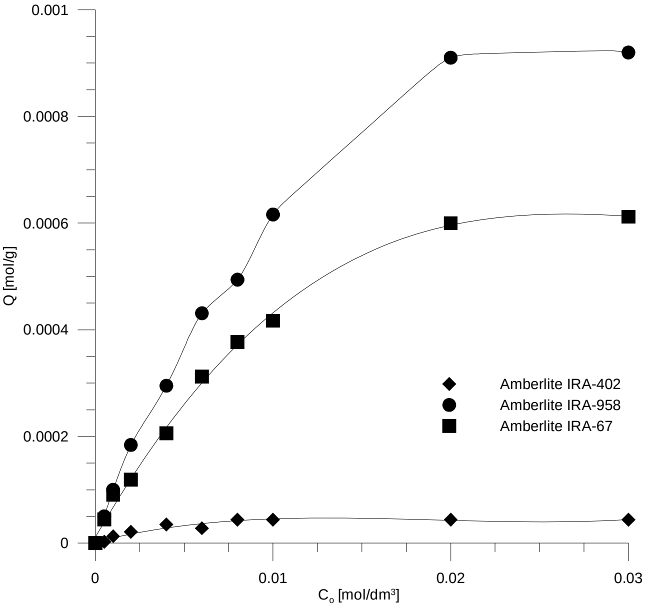

Fig. 2. Adsorption isotherms of Brilliant Yellow on the strongly (Amberlite IRA-402 and Amberlite IRA-958) and weakly (Amberlite IRA-67) basic anion-exchangers.

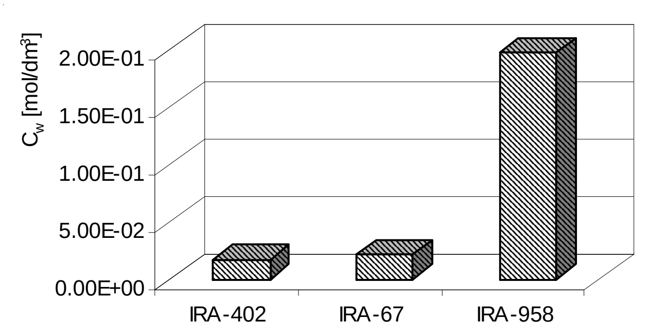

Fig. 3. Working ion exchange capacities for the anion-exchanger of various basicity (Amberlite IRA-402, Amberlite IRA-958, Amberlite IRA-67).

3.2. *Effect of initial concentration on adsorption of Brilliant Yellow*

As follows from the results, the percentage uptake of BY depends on the phase contact time as well as on the initial concentration of the azo dye for all used anion exchangers. Decrease in sorption of the dye is observed with the increase of initial concentration in the aqueous solution from 1×10^{-4} mol/dm³ to 1×10^{-2} mol/dm³. It was found that 100% removal was achieved at lower concentrations. Equilibrium uptake of Brilliant Yellow in the solutions of the initial concentration 1×10^{-4} mol/dm³ and 5×10^{-4} mol/dm³ was achieved within 30 min for strongly and weakly basic anion-exchangers (Fig. 4). The recovery factors of BY are relatively higher for the anion exchangers of acrylic-divinylbenzene matrix compared with those for styrene-divinylbenzene Amberlite IRA-402.

3.3. *Influence of pH and temperature*

The effect of pH on the recovery factors of Brilliant Yellow on the strongly and weakly basic anion-exchangers was investigated in the range 1–14. The values of recovery factors are very high, over 86% of the uptake was reached after 30 min. As can be seen from Fig. 5, the acidity effect on BY sorption is not so significant as expected. This supports our conclusion that Brilliant Yellow sorption depends mostly on the negatively charged dissociated sulpho-groups, although the van der Waals interactions between the resin matrix and the aromatic structure of the dye cannot be excluded.

Fig. 6 shows the uptake of Brilliant Yellow as a function of temperature under static conditions. % *R* of BY slightly increases with the increasing temperature up to 30°C for Amberlite IRC-402 of the styrene-divinylbenzene matrix. The values under discussion are relatively high (over 99%) in the temperature range from 20° to 60°C for the anion-exchangers of acrylic-divinylbenzene matrix.

3.4. *Recovery factors of Cu(II), Co(II) and Ni(II) using the modified anion-exchangers*

The modified anion-exchangers were used for recovery of Cu(II), Co(II) and Ni(II) ions from the chloride

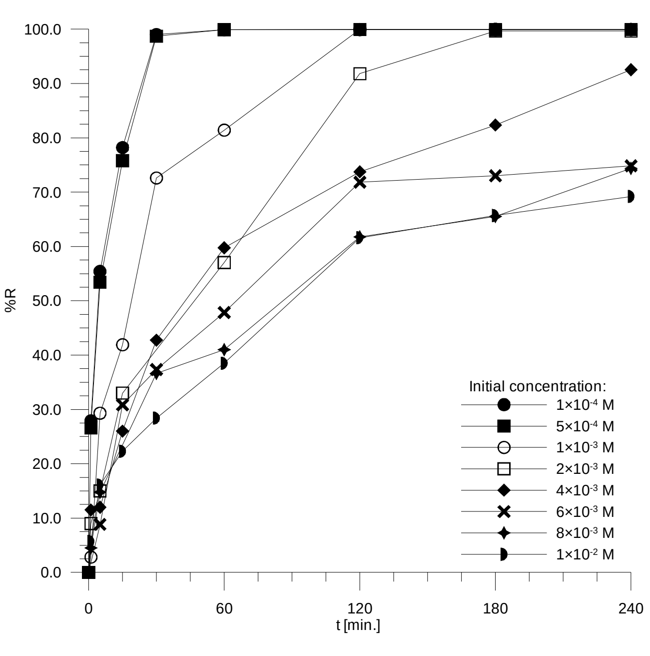

Fig. 4. Influence of Brilliant Yellow initial concentration and phase contact time on the recovery factors using Amberlite IRA-958.

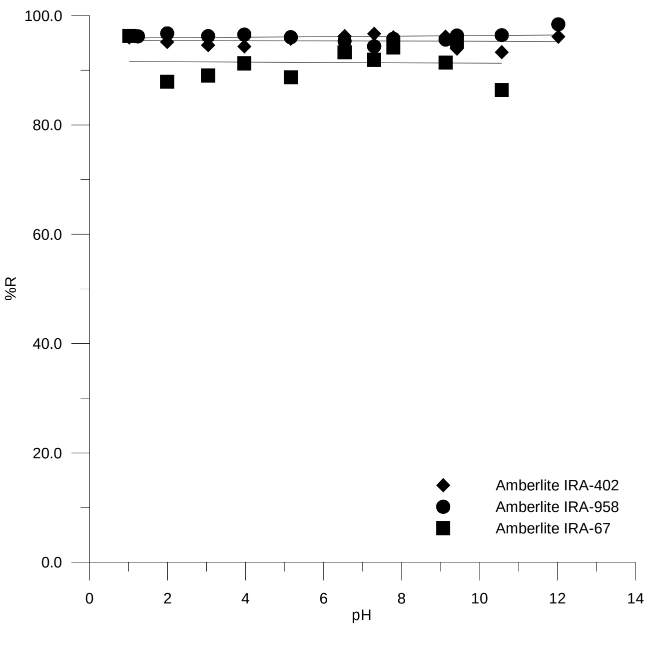

Fig. 5. Influence of pH on the recovery factors of Brilliant Yellow (phase contact time — 30 min, 0.2 g of the anion-exchanger, initial concentration — 1×10^{-4} M) using the anion-exchangers of various basicity.

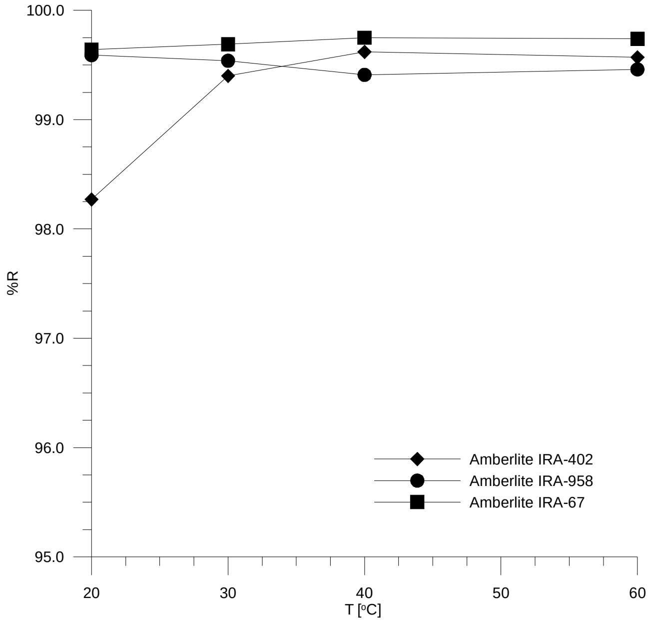

Fig. 6. Effect of temperature on the recovery factors of Brilliant Yellow (phase contact time — 30 min, 0.2 g of the anion-exchanger, initial concentration — 1×10^{-4} M) using the anion-exchangers of various basicity.

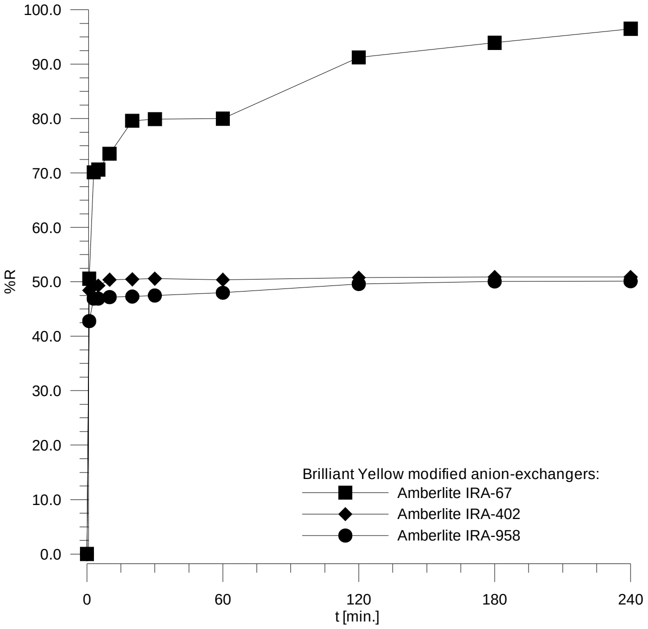

Fig. 7. Influence of phase contact time on the recovery factors of Cu(II) ions using the strongly and weakly basic anion-exchangers modified by means of BY.

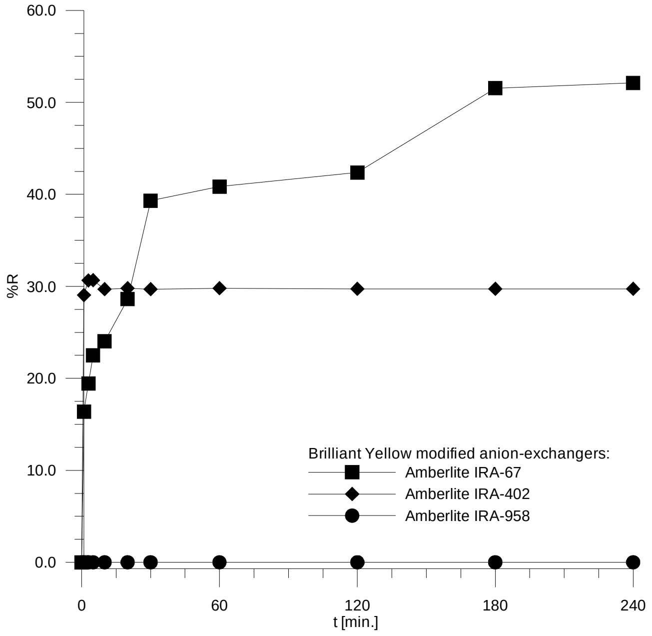

Fig. 8. Influence of phase contact time on the recovery factors of Co(II) ions using the strongly and weakly basic anion-exchangers modified by means of BY.

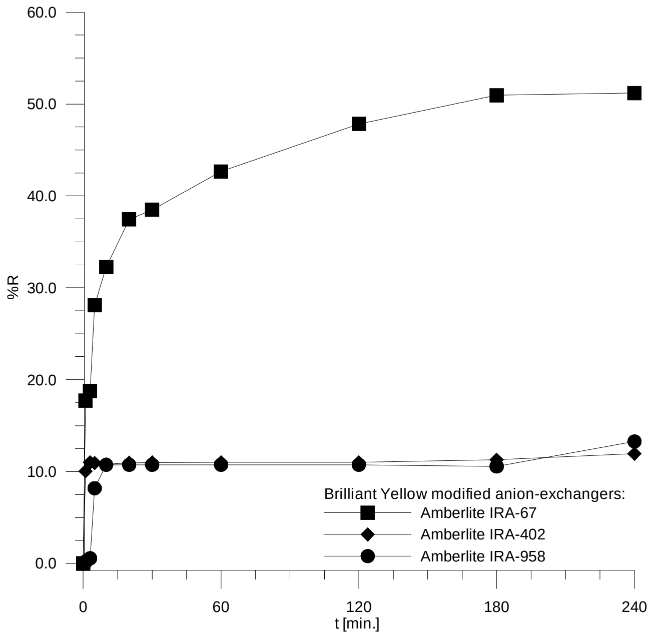

Fig. 9. Influence of phase contact time on the recovery factors of Ni(II) ions using the strongly and weakly basic anion-exchangers modified by means of BY.

solutions as shown in Figs.7–9. From the values of %*R* the studied anion exchangers of various basicity modified by means of Brilliant Yellow as far as their application is concerned in removal of these metal ions can be presented in the following series: Amberlite IRA-67 > Amberlite IRA-402 ≈ Amberlite IRA-958 for Cu(II) and Ni(II), Amberlite IRA-67 > Amberlite IRA-402 > Amberlite IRA-958 for Co(II).

4. Conclusion

- The research results indicate possible application of the strongly basic anion exchanger Amberlite IRA-958 and the weakly one Amberlite IRA-67 owing to their high selectivity in technologies of Brilliant Yellow recovery from tannery wastes, pulp-mill liquors and as well as wastewaters originating from textile industry.
- Brilliant Yellow forms a stable ion pair in the anion exchanger phase, it can be retained by means of a molecular mechanism (physical adsorption), too.
- The weakly basic anion exchanger Amberlite IRA-67 modified by means of BY as a prototype of chelating ion-exchanger can be also applied for Cu(II), Ni(II) and Co(II) ions recovery from wastewaters and in their trace analysis.
- Finding the most suitable anion exchangers for the dye removal on a commercial scale requires a detailed economic analysis, determination of optimal conditions (e.g. phase contact time, type and amount of the resin used), investigations of their chemical and mechanical resistance as well as Brilliant Yellow sorption and desorption kinetics (more than 100 cycles of sorption/desorption).

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