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Evaluation of possibility of textile dye removal from wastewater by aqueous two-phase extraction

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ABSTRACT

Possibility of removal of textile dye from wastewater by extraction in aqueous two-phase system (ATPS) was studied in model solution of Acid blue 9. Partitioning of the dye in ATPSs composed of polyethylene glycol of different molecular weights (1,500, 6,000, and 10,000 g/mol) and several salts (ammonium sulfate, sodium sulfate, and sodium citrate) was investigated. Best results in respect of partitioning coefficient and concentration factor were obtained in polyethylene glycol 1,500/sodium citrate and polyethylene glycol 6,000/sodium citrate systems, respectively. Moreover, in selected ATPSs, the effect of tie-line length and volume ratio on partitioning parameters of Acid blue 9 was evaluated in order to determine conditions at which the highest possible removal of textile dye from wastewater could be achieved.

Keywords: Textile dye; Wastewater; Partitioning; Aqueous two-phase system

1. Introduction

Due to rapid industrialization, a lot of chemicals including dyes are manufactured and used in day-to-day life. Synthetic dyes are extensively used in textile, dyeing, paper printing, color photography, food, cosmetic, and other industries. Approximately, 10,000 different dyes and pigments are used industrially and over 0.7 million tonnes of synthetic dyes are produced annually, worldwide [1]. Effluents from the textile industry usually contain high concentrations of organic compounds and are characterized by strong color as well as high chemical oxygen demand and total organic carbon values [2]. During the dyeing process, 10–15% of the dye is lost in the effluent [3] and color is the first contaminant to be recognized in wastewater and the presence of very small amounts of dyes in water is highly visible and undesirable [4]. Discharge of wastewaters containing dyes into surface water bodies stops the reoxygenation capacity of the receiving water and cuts off sunlight, thereby upsets biological activity in aquatic life [2]. Moreover, some dyes can be toxic and/or carcinogenic to mammalian animals [5].

Azo-dyes which are used extensively in many industries are the largest class of synthetic dyes with a wide variety of color and structure [6]. Azo-bonds present in azo-dyes are resistant to breakdown, with the potential for the persistence and accumulation of high levels of dye in the environment [1]. Anionic azo-dyes, which include direct, acid and reactive dyes,

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are widely used due to their bright colors, their excellent coloring fastness and the easiness of application. However, wastewater containing anionic azo-dyes usually has a strong color, a high level of toxicity, and is generally nonbiodegradable. Thus, the removal of these pollutants from wastewater has rapidly become a matter of great interests and significant efforts have been put into the development of efficient and cost-effective treatment methods [7]. A number of physical and chemical processes are employed in decolorizing dye wastewater, including coagulation–flocculation [8–10], ozonation [11], biodegradation [12], oxidative degradation [13–15], and adsorption [3,5,16,17]. Some of these techniques decolorize wastewater by partially decomposing the dye molecules and thereafter leaving the harmful residues in the effluent [7].

One of the methods to overcome these drawbacks in textile dye removal from wastewaters could be the application of the aqueous two-phase systems (ATPSs) which is an environmentally safe and economically viable method [18]. There are a few studies published on a successful usage of the ATPSs for separation and extraction of the different dyes [18–20]. An ATPS is formed by mutual incompatibility of two polymers or a polymer and a salt in aqueous solutions. Spontaneous separation of the phases occurs beyond a critical concentration of these components, resulting in two phases, enriched with respect to one of the components. Separations conducted in ATPSs offer a great number of advantages over the conventional separation techniques. Among them the most relevant are rapid mass transfer due to low interfacial tension, rapid and selective separation, easiness of operation mode, and reliability in scale-up [21].

The aim of this work was to investigate partitioning of textile anionic azo-dye, Acid blue 9, in ATPS and to evaluate its possible application in dye removal. After selecting appropriate systems, influence of tie-line length (TLL), phase volume ratio, and pH on partitioning of the Acid blue 9 was determined. The two parameters on which this study was based on were yield of the Acid blue 9 in the top phase and residual concentration of dye in the bottom phase of the system. Namely, maximizing the yield of the dye in the top phase was important in respect of the efficiency of the dye removal and its possible reuse, while minimizing the concentration in the bottom phase was of crucial importance, due to its value represents dye concentration that remains after wastewater treatment. Moreover, the capacity and flexibility of the investigated ATPSs were tested at 10 times increased dye load in water.

2. Materials and methods

2.1. Materials

Polymers used in experimental work were polyethylene glycol 1,500 (PEG 1,500), polyethylene glycol 6,000 (PEG 6,000), and polyethylene glycol 10,000 (PEG 10,000). Salts that used to form two-phase systems with polyethylene glycols were sodium citrate, sodium sulfate, and ammonium sulfate.

Acid blue 9 was the dye used in the study and the molecular structure was presented in Fig. 1 [22].

The two-phase systems were prepared by mixing thoroughly the required quantities of polymer and salt with Acid blue 9 water solution. The total mass of the two-phase system was 10 g. The two phases were allowed to separate in graduated cylinder before sampling, and then the upper phase was carefully removed with a pipette, leaving a small amount at the interface. The lower phase was then sampled through the bottom of graduated cylinder. Samples of each phase were analyzed for dye concentration.

2.2. Analytical method

Concentration of Acid blue 9 in all samples was determined by measuring the absorbance in the separated phases at 628 nm, with corresponding blanks obtained from systems made with distilled water instead of the dye solution.

2.3. Experimental plan

First experiments were carried out with the aim of determination of the best systems for Acid blue 9 partitioning. Nine ATPSs were formed by combining all polyethylene glycols and salts. After selection of the most suitable systems, further analysis was carried out in order to evaluate the influence of the TLL, phase volume ratio (V_t/V_b), and pH on the dye

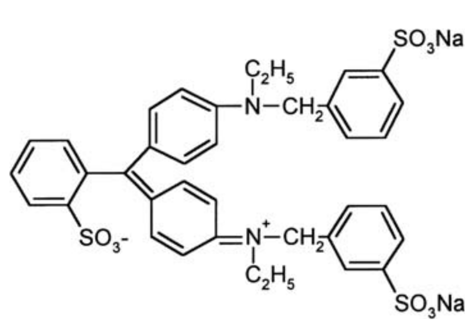

Fig. 1. Molecular structure of Acid blue 9.

removal by extraction in ATPS. All experiments were conducted with Acid blue 9 solution of 50 mg/L concentration. For investigation of the capacity of the applied systems dye solution of 500 mg/L was used.

2.4. Calculations

Acid blue 9 was distributed in the top phase of the applied APTS with the yield (Y_t):

$$Y_t = \frac{100}{1 + \left(K\frac{V_t}{V_b}\right)^{-1}}(\%) \tag{1}$$

where K is the partitioning coefficient, V_t is the volume of the top phase, and V_b is the volume of the bottom phase of the ATPS, while its ratio represents phase volume ratio.

Partitioning coefficient (K) from the Eq. (1) was calculated as follows:

$$K = \frac{C_t}{C_b} \tag{2}$$

where C_t and C_b are concentrations of the Acid blue 9 in the top and bottom phases of the ATPS (mg/L).

TLL was calculated by formula presented in the Eq. (3):

$$\mathrm{TLL} = \left[(x_{ti} - x_{bi})^2 + (x_{tj} - x_{bj})^2\right]^{1/2}(\%) \tag{3}$$

where x_{ti} and x_{bi} are concentrations in the top and bottom phases (w/w,%) of the polyethylene glycol, respectively, x_{tj} and x_{bj} are concentrations in the top and bottom phases (w/w,%) of the salt.

Concentration factor (CF) of the Acid blue 9 in the top phase of the ATPS was calculated as follows:

$$\mathrm{CF} = \frac{C_t}{C_0} \tag{4}$$

where C_t is concentration of the Acid blue 9 in the top phase of the ATPS (mg/L) and C_0 is concentration of the initial dye solution (mg/L).

3. Results and discussion

First set of experiments was conducted in order to determine the most suitable systems for Acid blue 9 partitioning, by combining all used polyethylene glycols and salts, leading to nine two-phase system compositions. Systems that were used for further investigations were chosen based on the highest efficiencies of extraction and CFs at constant phase volume ratio (data not shown). According to obtained results, systems containing polyethylene glycol 1,500 and 6,000 as polymer and sodium citrate as salt were chosen for further evaluation.

3.1. Influence of the TLL on the yield of the Acid blue 9 in the top phase and its concentration in the bottom phase of ATPS

Increasing the TLL (Eq. (3)) is reported to increase the hydrophobicity of the top phase in an ATPS and also the interfacial potential between the two phases [23]. During investigation of the influence of TLL on the partitioning of the Acid blue 9, the concentration of the phase constituents was chosen to ensure volume ratio amounted 1 in all experiments. Figs. 2 and 3 show results obtained for influence of the TLL on the yield of the Acid blue 9 in the top phase (Y_t) and its concentration in the bottom phase (C_b), for systems PEG 1,500/sodium citrate and PEG 6,000/sodium citrate, respectively.

It was observed that increasing in TLL favored partition of the dye in the top phase, in the both systems, which resulted in the increase of the yield in the top phase followed by decrease of concentration of the Acid blue 9 in the bottom phase. These results indicated possible application of the two-phase systems in the treatment of wastewater from textile industry considering that the efficiency of this technique in dye removal was higher than 80%, as it was requested by EU Directives [24].

3.2. Influence of the phase volume ratio on the yield of the Acid blue 9 in the top phase and its concentration in the bottom phase of the ATPS

Considering the phase volume ratio (V_t/V_b) is important in achieving the high yields in the top

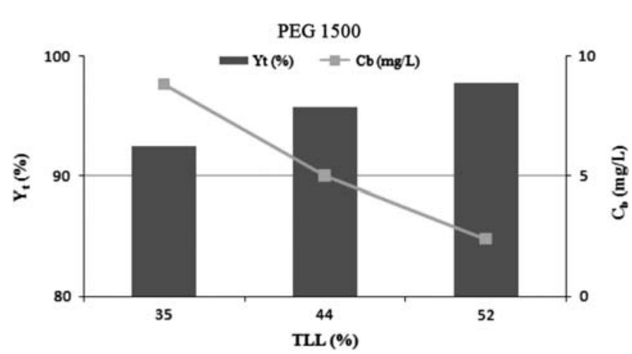

Fig. 2. Influence of the TLL on the yield of the Acid blue 9 in the top phase and its concentration in the bottom phase of PEG 1,500/sodium citrate system (phase volume ratio 1).

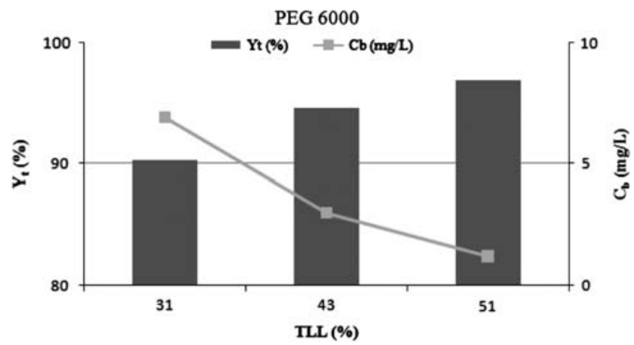

Fig. 3. Influence of the TLL on the yield of the Acid blue 9 in the top phase and its concentration in the bottom phase of PEG 6,000/sodium citrate system (phase volume ratio 1).

phase (Eq. (1)), its influence was examined. Results obtained for influence of the increase of the phase volume ratio along the longest examined tie-lines on the yield in the top phase and concentration of the Acid blue 9 in the bottom phase were presented in Figs. 4 and 5.

The lowest yield in the top phase and the highest concentration in the bottom phase were obtained at the phase volume ratio 1. In the system PEG 6,000/sodium citrate, Acid blue 9 had the highest yield in the top phase and the lowest concentration in the bottom phase at volume ratio 4.1. System PEG 1,500/sodium citrate showed the best result (the highest yield in the top and the lowest concentration in the bottom phase) at the volume ratio 3.

Because high CF (Eq. (4)) of dye in the top phase might open possibility for its reuse, in the following experiments this parameter was examined at phase volume ratio 0.5 in order to manipulate with smaller top phase volume. CFs that present measure of the dye concentrating along with yields in the top phase

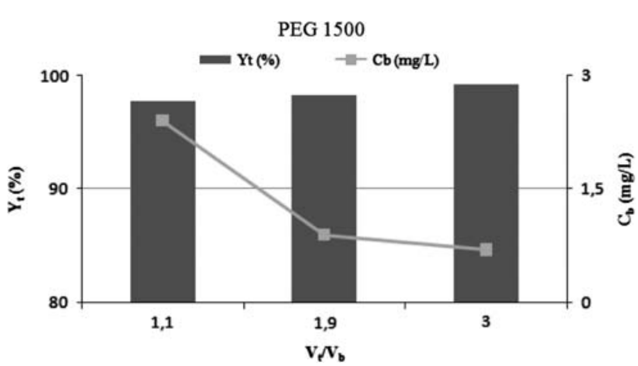

Fig. 4. Influence of the phase volume ratio on the yield of the Acid blue 9 in the top phase and its concentration in the bottom phase of PEG 1,500/sodium citrate system (TLL 52%).

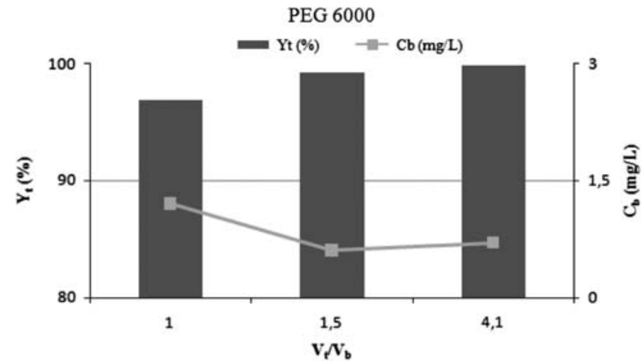

Fig. 5. Influence of phase volume ratio on the yield of the Acid blue 9 in the top phase and it concentration in the bottom phase of PEG 6,000/sodium citrate system (TLL 51%).

(Y_t) and concentrations in the bottom phase (C_b) were listed in Table 1 for both investigated ATPS.

It can be observed that at even decreased top phase volume, concentrating of the Acid blue 9 without yield decrease in the top phase and increase of dye concentration in the bottom phase were achieved in both investigated systems. Hence, achieved concentrating of the Acid blue 9 could increase potential of the system application not only for dye removal, but also for its possible reuse.

3.3. Influence of the pH value of the Acid blue 9 solution on its yield in the top phase and concentration in the bottom phase of the ATPS

Value of pH could influence partitioning of the Acid blue 9 by affecting molecule net charge and thus it could affect partitioning towards the phases of the systems. All previous experiments were conducted without changing the dye solution initial pH which was 6.7. In experiments examining influence of pH on the partitioning of the Acid blue 9, three pH values were applied: 4.7, 5.7, and 8.7 at the highest volume ratios and the longest tie-lines. Results for pH influence on the partitioning of the dye in systems PEG 1,500/sodium citrate and PEG 6,000/sodium citrate were presented in Figs. 6 and 7, respectively.

It can be seen that at pH value lower than pH of the dye solution, the top phase yields are slightly lower while concentrations in the bottom phases were higher than the ones obtained in experiments without pH correction, for both systems. As far as pH value higher than the initial pH of the dye solution, for both applied systems, it can be concluded that it had negative effect both on the top phase yields and remaining concentrations, especially on the concentration in the

Table 1
Yields of Acid blue 9 in the top phases and its concentrations in the bottom phases of the PEG 1,500/sodium citrate and PEG 6,000/sodium citrate systems at phase volume ratio 0.5

ATPS	V_t/V_b	CF	Y_t (%)	C_b (mg/L)
PEG 1,500/sodium citrate	0.5	2.05	99.33	0.3
PEG 6,000/sodium citrate	0.5	1.90	97.67	1.0

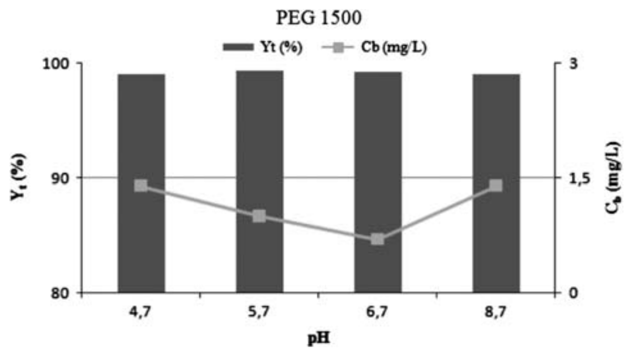

Fig. 6. Influence of the pH value of the initial solution on the yield of the Acid blue 9 in the top phase and its concentration in the bottom phase of PEG 1,500/sodium citrate system (TLL 52%, phase volume ratio 3.0).

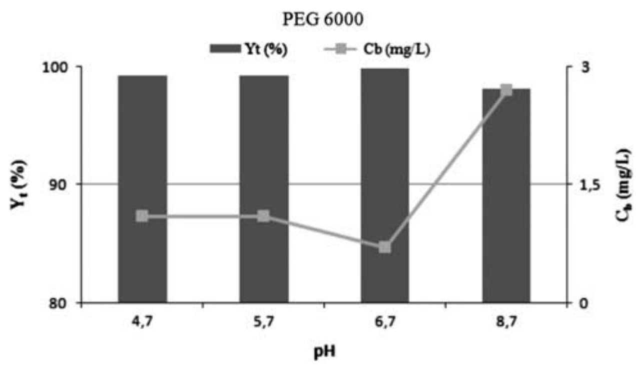

Fig. 7. Influence of the pH value of the initial solution on the yield of the Acid blue 9 in the top phase and its concentration in the bottom phase of PEG 6,000/sodium citrate system (TLL 51%, phase volume ratio 4.1).

bottom phase of the PEG 6,000/sodium citrate system. Presented results indicated that pH should not be corrected and the best partitioning of the Acid blue 9 was achieved at the natural pH of the dye solution which is environmentally beneficial.

3.4. Capacity and flexibility of the systems for removal of the Acid blue 9

ATPSs are known to be media enabling separations characterized by parameters which are reliable to scale-up [23]. Hence, the system's ability to remove dye at 10 times higher concentration (500 mg/L) than the one applied in the previous experiments was investigated. Results obtained for Acid blue 9 extraction from the initial solution having concentration of 500 mg/L for both systems at phase volume ratio 1 (at the longest tie-lines) in comparison to one with 10 times lower initial concentrations are presented in Table 2.

It can be concluded that both systems retain capacity to remove Acid blue 9 even at 10 time higher concentration, without significant loss in the yield in the top phases or without increase of the dye concentrations in the bottom phases of the investigated systems. In the system PEG 1,500/sodium citrate at higher dye concentration the higher yield in the top phase was achieved, while increase of the initial concentration of the Acid blue 9 for 10 times was followed by only two times increase in its concentration in the botom phase of this system.

This indicate that applied systems had capacity to remove high concentrations of the Acid blue 9 from the solution with very high yields (over 95%) in the

Table 2
Yields of Acid blue 9 in the top phases and its concentrations in the bottom phases of PEG 1,500/sodium citrate and PEG 6,000/sodium citrate systems at different initial dye concentrations

Acid blue 9 initial solution concentration (mg/L)	PEG 1,500/sodium citrate Y_t (%)	C_b (mg/L)	PEG 6,000/sodium citrate Y_t (%)	C_b (mg/L)
50	97.71	2.4	96.88	1.2
500	98.85	5.0	95.64	22.4

top phase leaving dye in the bottom phase at low concentrations.

4. Conclusion

Results presented in this study indicated that ATPSs composed of the PEG 1,500 and sodium citrate and PEG 6,000 and sodium citrate could be used for efficient removal of the Acid blue 9 from solutions having concentration up to 500 mg/L. High yields obtained in the top phase of the system and low dye concentrations obtained in the bottom phase along with high CFs supported this statement. Achieved Acid blue 9 dye removal in the yield higher than 95% was satisfactory in respect of our local government regulation [25] as well as EU Directives [24] that recommend use of techniques that would be able to remove more than 80% of the polluting dye. Moreover, phases of ATPSs are environmental friendly and the presence of polyethylene glycol in the top phase in which Acid blue 9 was concentrated should not influence its dyeing ability when reused.

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