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SOLVENT SUBLATION OF INDIGO CARMINE FROM WATER

ФЛОТОЭКТРАКЦИЯ ИНДИГО КАРМИНА ИЗ ВОДЫ

Summary. *Indigo carmine (IC, $C_{16}H_8N_2Na_2O_8S_2$), an anionic dye, was removed from aqueous solutions by solvent sublation of an IC–hexadecylpyridinium bromide (HPB) complex (sublate) into octanol. The effects of the following parameters on solvent sublation were experimentally studied: the molar ratio of HPB: IC, pH of aqueous phase, the removal process duration, type and volume of organic solvent. The initial dye concentration was 10 mg/dm^3.*

It was found that the process should be conducted under such conditions: pH 5, solvent – octanol, Schott filter nominal pore size – 100 μm, molar ratio of HPB: IC = 1:1, process duration – 20 min. According to obtained results the highest level of IC elimination was reached within the experiment equals 94,38±0,34 %.

Key words: *solvent sublation, removal ratio, sublat.*

Аннотация. *Индиго кармин (ИК, $C_{16}H_8N_2Na_2O_8S_2$), анионный краситель, извлекали из водного раствора флотоэкстракцией ИК – гексадецилпиридиний бромид (ГПБ) комплекса (сублат) в октанол. Экспериментально было исследовано влияние на флотоэкстракцию следующих параметров: молярное соотношение ГПБ: ИК, рН водной фазы, продолжительность процесса извлечения, природа и объем органического растворителя. Исходная концентрация красителя 10 мг/дм^3.*

Было получено, что процесс следует проводить при следеющих условиях: pH 5, экстрагент — октанол, размер пор фильтра Шотта 100 мкм, молярное соотношение ГПБ: ИК = 1:1, продоолжительность процесу 20 мин. Согласно полученным результатам, наиболее высокая степень извлечения ИК в эксперименте составляет 94,38±0,34 %.

Ключевые слова: *флотоэкстракция, степень извлечения, сублат.*

There are different methods of wastewater treatment that provide either elimination or destruction of dyes such as: chemical processes (the use of Fentons reagent, ozonation, photocatalytic decolourization, electrochemical destruction), physical treatments (adsorption, membrane filtration, ion exchange, electrokinetic coagulation, etc.) and microbiological decomposition [1]. However all these techniques are often too expensive for applying, ineffective or produce much sludge. Therefore the search for more effective, inexpensive and low-waste method for dyes remediation from water still remains actual. In this case, solvent sublation is a good alternative. In this special adsorptive bubble separation non-foaming technique some organic solvent is placed on the top of aqueous phase and is used to collect the sublate adsorbed on the bubble surfaces of an ascending gas stream. This method with its advantages of simultaneous separation and concentration has recently attracted much attention in many fields. Based on the previous reports and recent researches the following advantageous of solvent sublation can be outlined: 1) high separation efficiency; 2) high concentration coefficient; 3) low dosage of organic solvent; 4) soft separation process; 5) simple operation and equipment. Moreover, this technique provides the possibility of the further dye recovery after its elimination [2–3].

The removal of IC, an anionic dye from aqueous solution by solvent sublation was studied. IC can cause some environmental problems, the search of a simple and effective removal method is necessary. In this work the efficiencies of solvent sublation with some conventional separation methods were compared.

The solvent sublation process took place in glass column. It was 50 cm in length with an initial diameter of 3,5 cm and had 2 access ports. The gas bubbles were generated in a Schott filter with porosity of 100 µm. Compressed nitrogen was supplied by the gas cylinder and moved through the humidifier and the filter to the bottom of the solvent sublation column. Gas rate was measured by flow meter. To obtain dye concentration in the aqueous phase, the sample solution was withdrawn from the top access port for analysis. Reagent-grade HPB was used as a collector without further purification. Reagent grade IC and the other reagents were all analytical grade. For the solvent sublation running, HPB was added to the sample solution (250 cm³) to form the dye-surfactant complex; the solution contained 10 mg/dm³ IC and was poured into the sublation column; 5 cm³ of octanol was added immediately; then the timer was started and the samples of aqueous solution were taken for analysis at specified times. The pH of the solution was measured with a pH-meter Portlab 102. UV-visible spectra of the sample solutions were measured with a scanning spectrophotometer Portlab 501. Parameters, which affect the solvent sublation process can be classified as those, that affect the aqueous and organic solutions and those, which are operational factors. Parameters of the first group are: aqueous phase composition (pH, ionic strength, presence of various species), organic phase composition (organic solvent: type and volume). The operational parameters are: gas flow rate, temperature, process duration. PH of the aqueous solution is a very important factor because it determines the presence of ionic species, which are involved in solvent sublation process. Such processes as hydrolysis, complex formation and precipitation

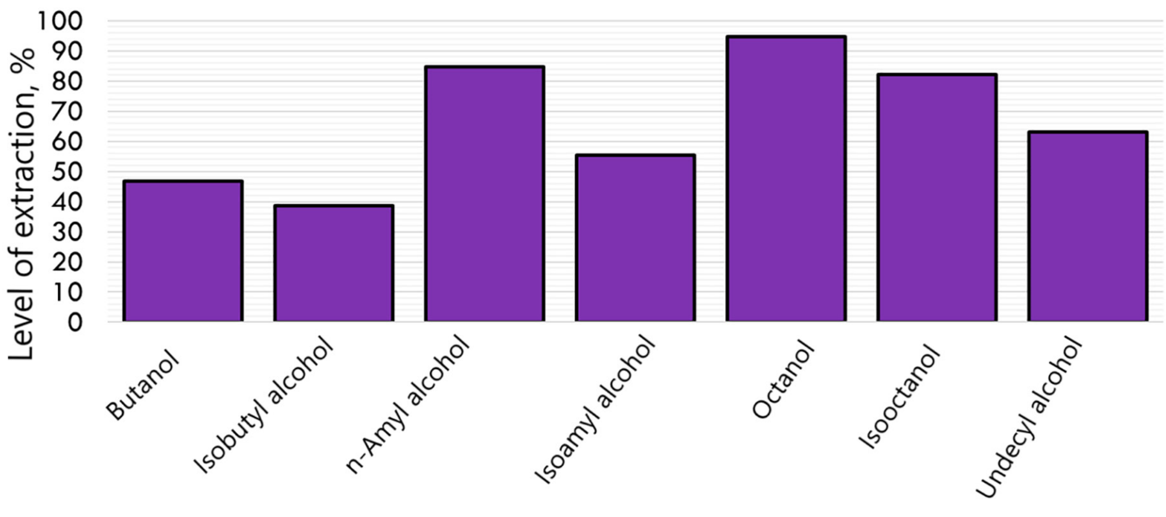

Fig. 1. The variation of IC removal efficiency in dependence of the organic solvent type

of insoluble substances are governed by pH values of aqueous solutions. The presence of surfactant is also very important factor for solvent sublation because usually it makes extracted ion-pairs more hydrophobic. In addition, surfactants tend to reduce the surface tension of aqueous solution and decrease the size of bubbles generated in the sparger. Hexadecyl-pyridinium-bromide was used as the surfactant in all cases because it showed high efficiency in the process of IC removal by solvent sublation during previous researches. It's known, the higher sublate solubility in organic layer is the bigger efficiency of dye removal is obtained (Fig.1). In this research different organic compounds were investigated to find out the proper one.

In the solvent sublation system, octanol was chosen as the organic solvent, which has a high solubility of the IC– HPB, immiscible to the aqueous phase, low-aqueous-organic solvent interfacial tension, nontoxic, and nonvolatile.

Therefore in this study the experiment was conducted under the maximum permitted gas flow rate condition (40 sm^3/h). At higher gas flow rates, the oil-water interface can be drastically disrupted and some drops of the top organic layer can return back to solution.

Dye concentration in the aqueous phase was measured every 5 minute for 30 minutes. As graph shows (Fig. 2) the optimum process duration was equal to 20 minutes with 94 % IC removal accordingly.

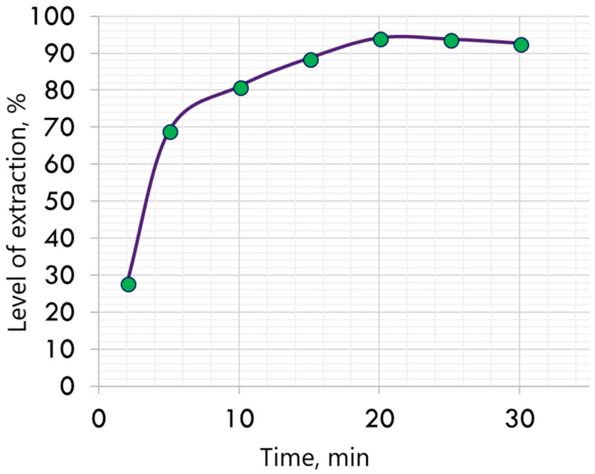

Fig. 2. The variation of IC removal efficiency in dependence of the elapsed time

A series of experiments were carried out using solutions at pH with diferent HPB to IC molar ratios while keeping the airflow rate at 40 cm^3/min. The efect of concentration HPB on the solvent sublation of IC is shown in Fig.3. It was found that the efciency of separation improved with the increase of molar ratio of surfactant to IC, and that the efciency became highest at 1:1,5. At a smaller concentration of the surfactant, the rate of removal was slower and the level of the residual dye greater, presumably due to incomplete formation of a dye-surfactant complex.

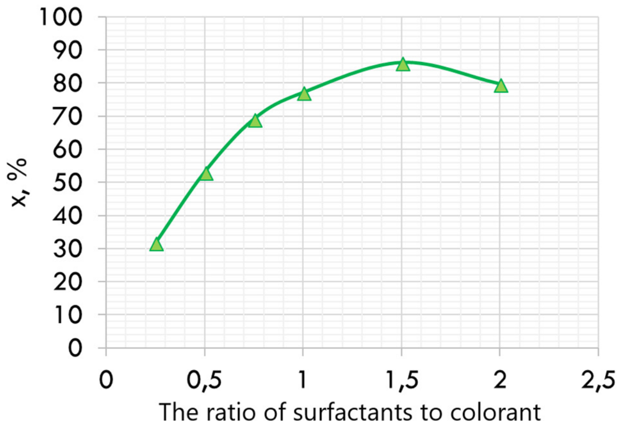

Fig. 3. The dependence of IC removal efficiency on the molar ratio of HPB to IC

However, when the ratio was greater than 1:1,5, the rate of solvent sublation was smaller and the removal efficiency was slower, presumably due to the competition for the bubble surface by the excess surfactant ion with the dye-surfactant complex. It was observed that the excess surfactant could also cause the emulsification of the octanol (which was observed during the solvent sublation process with a larger excess of surfactant), and the dye-surfactant complex in the octanol was constantly dispersed back into the solution to decrease the separation significantly.

The effect of pH on the removal of IC — HPB in the process of solvent sublation is shown in Fig. 4. The removal rate and removal efficiency of IC increased with the increase of the value of pH, and reached the most high removal efficiency at the natural pH value, then decreased with the increase of the pH value. At the natural pH value over 90 % of IC was removed from the solution by solvent sublation in 5 min. But at lower pH value, the removal rate and efficiency decreased.

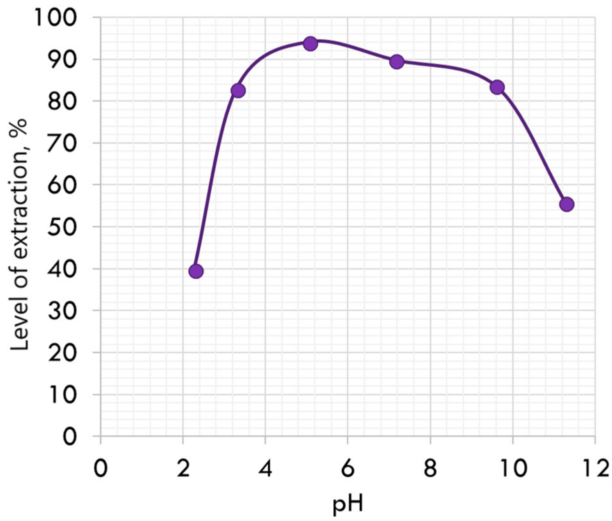

Fig. 4. Effect of pH on solvent sublation

To sum up, within this report contemporary state of water pollution problem, caused by synthetic dyes was analysed, covering the main methods that are typically used for dyes decomposition and remediation. Solvent sublation was proposed as an effective alternative. The main principles of Indigo carmine removal from water by solvent sublation were investigated. The following major parameters and their influence on Indigo carmine removal from water were researched in detail: type and volume of organic solvent, the molar ratio of surfactant to dye, pH. The highest dye removal was obtained in the case of octanol used as the solvent. The initial dye concentration was 10 mg/dm^3.

It was found that the process should be conducted under such conditions: the pH 5–5,5, solvent — octanol, molar ratio dye: surfactant — 1:1,5, process duration — 20 min. The recovery efficiency was 94,38±0,34 %. Attained results can be used in further studies.

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