# The investigation of Bromphenol blue removal from water by solvent sublation

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## Abstract

In this research which complements the previously published works of this team on dyes removal, solvent sublation was employed in order to remove such dyestuff as Bromphenol Blue from simulated effluents. The aim of the work was to study the main principles of Bromophenol blue removal from water by solvent sublation. Bromophenol blue (BB), an anionic dye, was removed from aqueous solution by solvent sublation of a BB – hexadecyl-pyridium-chloride (HPC) complex (sublate) into isopentanol. The effects of the following parameters on the solvent sublation were experimentally studied: the molar ratio of HPC to BB, pH of the aqueous phase, the removal process duration, type of organic solvent and the size of bubbles generated in the sparger. By making second order central composite orthogonal design and deriving mathematical model with the aid of MS Excel 2003 it was found that satisfied efficiency of depicted process can be attained in a case of carrying it out under the following optimum conditions: temperature 10ºC, surfactant/dye molar ratio 1.94:1; process duration – 15.3 min. The check of model adequacy proved that it can accurately describe the process and can be used for further simulations. According to obtained results the highest level of BB elimination reached within the experiment was equal to 97.5%.

## Аннотация

Представленые результаты являются логическим продолжением исследований по флотоэкстракционному извлечению красителей на примере модельных растворов бромфенолового синего (БС). Целью данной работы было изучение основных закономерностей удаления БС флотоэкстракцией. БС, анионный краситель, извлекался из водного раствора флотоекстракцией комплекса БС–хлорид гексадецилпиридиния (сублат) в изопентанол. Экспериментально было исследовано влияние на флотоекстракцию следующих параметров: мольное соотношение ПАВ:БС, рН водной фазы, длительность процесса извлечения, природа органического растворителя и размер сгенерированных пузырьков. Путем построения центрального композиционного ортогонального плана второго порядка и выводом математической модели с помощью MS Excel 2003 было определено, что удовлетворительная эффективность описанного процесса может быть достигнута в случае проведения его при таких оптимальных условиях: температура 10 ºC, мольное соотношение ПАВ:БС = 1,95:1, продолжительность процесса – 15,3 мин. Проверка адекватности модели подтвердила, что она удовлетворительно описывает процесс и может использоваться в дальнейших исследованиях. Согласно полученным результатам, самая высокая степень извлечения БС, достигнутая в ходе эксперимента, равна 97,5%.

**Keywords:** Dye, bromphenol blue, hexadecyl-pyridium chloride, mathematical model, solvent sublation, spectrophotometry.

**Introduction**

It's well-known that water is a unique substance which extinction will cause the death of every living organism. Despite the key role of water in the human life these days the worsening of nature water quality is increasing rapidly. Annually around 450 m$^3$ of effluent, containing wide range of pollutants, is discharged directly into the rivers and other surface water basins. More than a half of this amount doesn't undergo any effective pretreatment.

Unfortunately Ukraine doesn't remain beyond this ecological problem, moreover, it endures its exacerbation phase. According to international standards, mainly all of our big rivers and their tributaries, belong to the category of polluted or highly polluted waters. There are numerous rivers where the content of one or several impurities exceeds the maximum allowable concentration (the M.A.C.) in dozens of times, for example, the Dnipro, the Desna, the Styj River, the Siverskyj Donets and others.

The accumulation of toxic effluent components is a considerable hazard to water resources potential of the country. It particularly relates to waste water pollutants belonging to II-IV hazard classes such as organic dyes and diluents.

The main sources of water pollution by dyes are the following: textile industry, chemical plants, cellulose and paper industry and pharmaceutical industry. It is assumed that during dye production the loss of target product is nearly 1–2% and in the case of dye usage 1–10% loss occurs. For reactive dyes, this figure can be about 4% (Forgacs et al., 2004). Perhaps, this is caused by dye dilution in the water used for its synthesis and the amount of such water is enormous: it takes approximately 100 – 225 tons of water to produce 1 ton of dye (Nesterova, 2010).

Textile industry also stands out, as it yields a large amount of effluents. It is estimated that about 10-15% of dyes are released into processing water during different procedures (L and V.P., 2010).

So it's obvious that the discharge of such raw effluent into the surface water entails high-level pollution thus in natural water dyes concentrations highly exceed affordable limits (0.05 – 0.25 мг/l).

Due to complicated chemical structure of synthetic dyes they can't be biochemically decomposed in aqueous systems therefore local treating plants are not able to cope with this problem. Synthetic dyes are also extremely hazardous pollutants of natural environment due to the effect of potentiation. As a consequence, the result of such interactions is often unexpected.

Entering the environment dyes easily colour the water and the surrounings consequently causing unfavorable estetic impression, worsening water organoleptic properties. In addition, dyes can significantly effect the photosynthesis ability of the water inhabitants by decreasing water transparency. Dyestuff can be toxic for some flora and fauna species because of aromatic rings and chlorine substituents in their structure (L and V.P., 2010). This can lead to total extinction of water living organisms, self-treatment processes disruption and human intoxication.

Hence synthetic dyes can cause significant environmental pollution and bring a serious risk factor for human diseases too.

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 (Robinson et al., 2001). 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 placed on the top of aqueous phase 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 (Bi et al., 2010).

Moreover, this technique provides the possibility of the further dye recovery after its elimination.

The objective of this research was to investigate the main principles of Bromphenol blue remediation from water by solvent sublation technique.

To rich this goal the next tasks had to be completed:

1) to study major parameters and their influence on the solvent sublation process;
2) to build a mathematical model that could adequately describe the process;
3) to determine optimum conditions which could assure attaining satisfactory results.

**Materials and methods**

The scheme depictured below was used to carry out solvent sublation process (Fig.1).
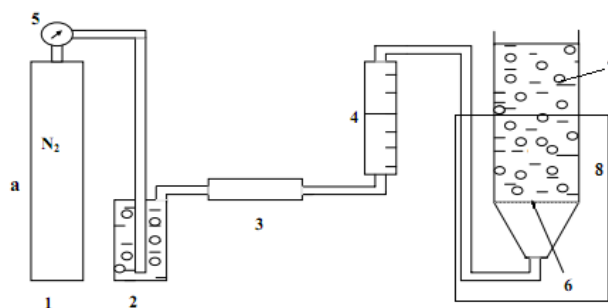


**Figure 1** Flowsheet of the experimental unit

1 – gas cylinder; 2 – humidifier; 3 – filter; 4 – gas flow rate; 5 – pressure meter; 6 – Schott filter; 7 – solvent sublation column; 8 – thermostat.


The solvent sublation process took place in glass column 7. It was 42 cm in length with an initial diameter of 3.3 cm and had 2 access ports. The gas bubbles were generated in a Schott filter of 16 µm porosity. Changing the porosity of the gas sparger (16, 40,100 and 160 µm), different bubble sizes were also created, thus altering the surface area of gas bubbles. Compressed nitrogen was supplied by the gas cylinder 1 and moved through the humidifier and the filter to the bottom of the solvent sublation column. Gas rate was measured by flow rate meter 4. Thermostat was used to maintain system temperature near the desired setpoint.

To obtain dye concentration in the aqueous phase, the sample solution was withdrawn from the top access port for analysis.

Reagent-grade HPC was used as a collector without further purification. Reagent grade BB and the other reagents were all analytical grade.

For the solvent sublation running, HPC was added to the sample solution (250 mL) to form the dye-surfactant complex; the solution containing $1.5 \times 10^{-5}$ mol/L (10 mg/l) BB was poured into the sublation column; and 5 mL isopentanol was added immediately; then the timer was started and the samples of aqueous solution were taken for analysis at a 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 at the maximum peak of 588 nm.

## Results and discussion

Parameters influencing the solvent sublation process can be classified as those, that effect 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, presence of different additives). The operational parameters are: gas flow rate and temperature.

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 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 (Sobianowska et al., 2009/2010).

Hexadecyl-pyridium-chloride (HPC) was used as the surfactant in all cases because it showed high efficiency in the process of BB 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. In this research different organic compounds were investigated to find out the proper one.

One of the crucial parameters is mean bubble radius that is formed by Schott filter.

Gas flow rate is also an important factor for solvent sublation process. According to previous publication (Lu et al., 2001), the increase of gas flow rate enhanced the removal efficiency due to mass transfer intensification. Therefore in this study the experiment was conducted under the maximum permitted gas flow rate condition (50 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.

## The effect of process duration on solvent sublation

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 15 minutes with 97.5% BB removal accordingly.
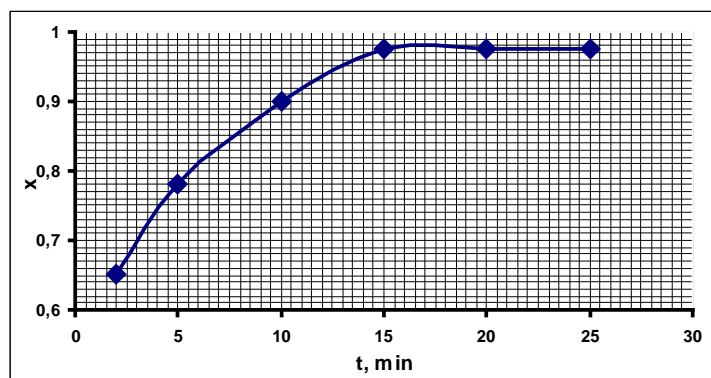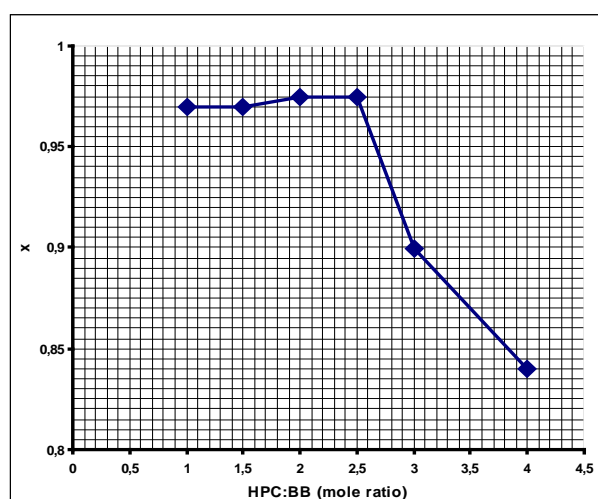
**Figure 2** The variation of BB removal efficiency in dependence on the elapsed time. HPC:BB (mole ratio) 2:1, pH 1,1, pore diameter 16 µm.


**The effect of the molar ratio of HPC to BB on solvent sublation**

HPC together with BB formed hydrophobic complex that interacted with gas bubbles. Then hydrophobic compound was levitated on a bubble surface to the top of an aqueous column where it encountered a solvent layer (isopentanol) to which the material was transferred as the bubbles moved through the solvent layer.

Results of this experiment are shown below (Fig.3).



**Figure 3** The dependence of BB removal efficiency on the molar ratio of HPC to BB. pH 1,1.


The graph shows that molar ratio HPC:BB 2:1 caused the highest dye remediation equal to 97.5% providing the lowest residual dye concentration in the water. The range of molar ratios HPC: BB from 1:1 до 1,5:1 didn't represent affordable results, perhaps due to incomplete formation of a dye-surfactant complex. When the ratio was higher than 2:1, the rate of solvent sublation was smaller and the removal efficiency was lower, presumably due to the competition of excess surfactant ion with the dye-surfactant complex for the bubble surface.

Large excess of surfactant can also cause the emulsification of the isopentanol thus the dye-surfactant complex in the isopentanol can constantly be dispersed back into the solution and the separation efficiency can decrease greatly (Lu et al., 2001).

**The effect of organic solvent nature on the process effectiveness**

Within this research the influence of such organic frame particularities as carbon chain length and the degree of branching in the carbon chain was investigated. The next compounds were used as the organic solvent: n-pentanol, isopentanol, 1-hexanol, 1-octanol and 2-octanol (Fig.4).
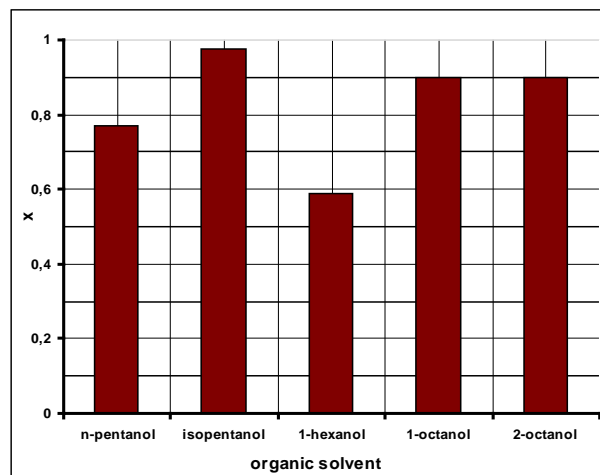


**Figure 4** The variation of BB removal efficiency in dependence on the organic solvent type. HPC:BB (mole ratio) 2:1, pH 1,1, pore diameter 16 µm.

The diagram shows that the highest BB removal equal to 97.5% was achieved by the use of isopentanol as an organic solvent. So, according to attained results, the branching of the carbon chain influenced the treatment process in the positive way, and the effect of normal structure of the carbon chain is diametrically different. For example, in the case of n-pentanol BB removal is much lower and is equal to 77 %. The first possible reason lies in the fact that probably there is much better solubility of dye-surfactant complex in organic solvent with higher degree of branching in the carbon chain. And possible easier holding of big-sized sublate by branched carbon skeleton solvent is the other reason. In the case of using n-hexanol the lowest dye elimination was obtained.

However depicted tendency can't adequately describe the behaviour of solvents which have longer carbon chains, for example, 8 or more carbon atoms. In such case both 1-octanol and 2-octanol retained practically equal amounts of dye.

Therefore the degree of carbon chain branching didn't play any essential role there. Either of these two isomers attained 90% of BB removal, but this efficiency is lower than in the case of isopentanol. This can be explained by difficulties of the sublate solubility or retaining within the solvent layer characterised by more complicated skeleton.

**The effect of the mean bubble diameter on the solvent sublation**

As it was previously mentioned, the size of bubbles generated in the sparger is one of the key factors in solvent sublation. Attained results are shown in Fig. 5.
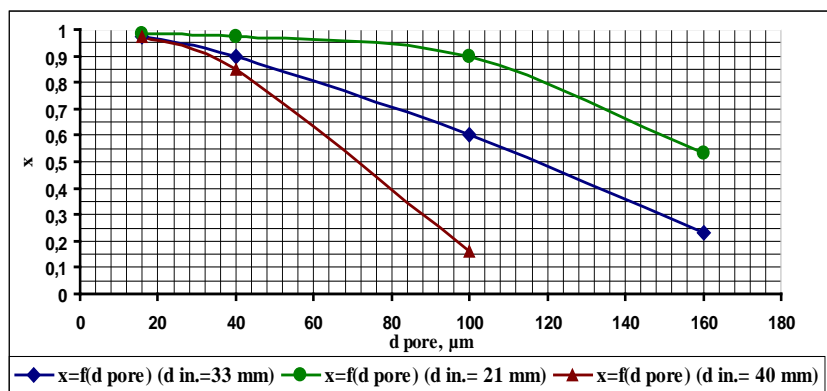
**Figure 5** The variation of removal efficiency in dependence on the bubble size. HPC:BB (mole ratio) 2:1, pH 1,1.

The graphs show that the removal efficiency increased with the decrease the of generated bubble diameter. The highest recoveries were obtained for all three columns with initial diameters 21, 33 and 44 mm in the case of applying Schott filter of 16 µm porosity x = 98.5, 97.5 and 97.5% respectively. Attained data proved that the bigger pore size was, the lower remediation efficiency it caused and the worst results were obtained in the case of the most massive gas bubbles: x=53, 23, 16%.

Bubble size reduction caused the increase of the interfacial area per unit volume of air (3/r), thus the bubble residence time also extended because smaller bubbles had lower rise velocities. Smaller bubbles also enhanced mass transfer from the liquid phase to the bubbles due to very large surface area per unit volume of air.

According to the represented graphs (Fig. 5) the decrease of the column initial diameter intensified the removal process. This can be explained by higher retention time of the bubble in the system.

**The effect of pH on solvent sublation**

Despite the results of the previous reports (Lu et al., 2001; Sobianowska et al., 2009/2010) this research revealed that in the case of BB removal pH of the aqueous phase slightly influenced the process run.

The results of the experiment are represented below (Fig. 6). The graphs show that the increase of pH reduced treatment efficiency. At pH 12 the lowest BB removal was detected: x = 96% that corresponds to the residual dye concentration in water equal to 0.4 mg/dm$^3$.
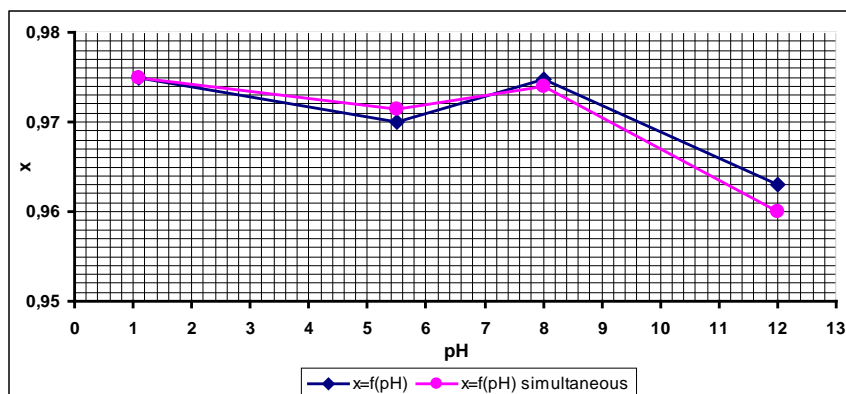


**Figure 6** The dependence of the BB removal efficiency on the pH value. HPC:BB (mole ratio) 2:1, $\tau$ =15 min.

Such behaviour can be explained by equilibrium established in aqueous solution:

$$B + A^- \xrightleftharpoons[OH^-]{H^+} HA + BH^+ \rightleftharpoons \left[ HA - BH^+ \right], \qquad (1)$$

where $B$ represents the HPC; $HA$, dye – Bromphenol blue; $A^-$, the deprotonated anion of BB; $BH^+$, protonated HPC cation.

According to the equation (1) the increase of the acidic pH drives the equilibrium toward a larger concentration of $BH^+$, which easily binds with $HA$ to form $\left[ HA - BH^+ \right]$. By contrast, the increase of the basic pH drives the equilibrium toward a larger concentration of $B$, which does not easily form dye-surfactant complex.

In spite of slight effect of pH on the BB removal observed throughout the experiment, the most proper pH value for efficient treatment was pH 1.1. Because it assured the lowest value of residual dye concentration 0.25 mg/l.

**Mathematical model deriving and the determination of optimum conditions**

Central composite orthogonal design (second order) was selected to derive mathematical model with the aid of MS Excel 2003. The following model was obtained:

$$Y = 66{,}22 + 0{,}43 \cdot Z_1 + 6{,}79 \cdot Z_2 + 2{,}59 \cdot Z_3 - 0{,}06 \cdot Z_1 \cdot Z_2 + 0{,}01 \cdot Z_1 \cdot Z_3 + 0{,}13 \cdot Z_2 \cdot Z_3 \qquad (2)$$
$$-0{,}02 \cdot Z_1^2 - 2{,}11 \cdot Z_1^2 - 0{,}07 \cdot Z_3^2,$$

according to the next definition: $Z_1$ - temperature factor; $Z_2$ - surfactant excess factor; $Z_3$ – process duration factor.

By deriving mathematical model, represented above, it was found that the maximum efficiency of depicted process can be attained in a case of carrying it out under the following optimum conditions: temperature 10ºC, surfactant/dye ratio 1.94:1; process duration – 15.3 min.

The check of the model adequacy proved that it can accurately describe the process and can be used for further simulations. The maximum relative standard deviation was equal to 4,7%.

**Conclusions**

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 Bromophenol blue removal from water by solvent sublation were investigated. The following major parameters and their influence on Bromphenol blue removal from water were researched in detail: pH, type of organic solvent, the mean bubble diameter, gas flow rate and molar ratio of surfactant to dye.

Acidic pH, fine bubble radius had a positive effect on the removal efficiency. The increase of gas flow rate up to 50 sm$^3$/min also enhanced the treatment. The highest dye removal was obtained in the case of isopentanol used as the solvent. The initial dye concentration was 10 mg/dm$^3$.

The second order experiment statistical model was derived with the use of central composite orthogonal design. The check of model adequacy proved that it can accurately describe the process and can be used for further simulations. The maximum relative standard deviation was equal to 4,7%.

To assure attaining the maximum treatment efficiency the next optimum conditions were determined: temperature 10°C, surfactant/dye ratio 1,94:1; process duration – 15.3 min. It was found that the process should be conducted under such conditions: pH 1.1, solvent – isopentanol, Schott filter nominal pore size – 16 µm, molar ratio surfactant:dye – 2:1.

The recovery efficiency was 97.5% and the corresponding residual Bromphenol Blue content in the aqueous phase was equal to 0.25 mg/dm$^3$. Attained results can be used in further studies.

Attained results can be used in further studies.

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