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LIQUID-LIQUID EXTRACTION AND ITS APPLICATION FOR THE REMOVAL OF BRILLIANT GREEN FROM AQUEOUS SOLUTION. A Simple Undergraduate Lab Oriented Project

Aplicación de extracción líquido-liquido para separación del verde brillante de las soluciones acuosas. Proyecto basado en laboratorios

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Abstract

In the undergraduate Environmental Analytical Chemistry course, the students are taught various separation techniques like GC, column adsorption chromatography, HPLC, solvent extraction, etc. Considerable emphasis is given to the application to these separation techniques for the removal of pollutants from wastewater. These include toxic heavy metal ions like Hg^{2+}, Pb^{2+}, etc. and organic contaminants such as the dyes and other Polycyclic Aromatic Hydrocarbons (PAH). These separation techniques are then coupled with a suitable instrumental method of analysis.

Keywords: Liquid-Liquid Extraction, removal of organic dyes, laboratory practice

Resumen

Hay varios proyectos en nuestro plan de estudios : proyectos orientados a estudios, orientados al laboratorio, proyectos computarizados y proyectos especiales. Para proyectos orientados al laboratorio

para estudiantes, se asignan los estudios de las separaciones de los colorantes orgánicos y el objetivo de estos trabajos es encontrar los métodos convenientes de separaciones en la solución acuosa. La mayoría de los colorantes sólo se separan por los métodos de adsorción, existen pocos ejemplos de aplicación de otras técnicas de separación, como la extracción de líquido-líquido. Esta técnica de la separación muestra una aplicación práctica de los conceptos teóricos discutidos en el aula. En el trabajo se discuten los resultados de aplicación de este método de laboratorio.

Palabras clave: extracción líquido-líquido, separación de colorantes , trabajos de laboratorio

Introduction

1. The projects in our undergraduate curriculum are classified as Study Oriented Project (SOP), Lab Oriented Project (LOP), Computer Projects and Special Projects. As an undergraduate LOP, a study on the removal of an organic dye (Brilliant Green), was assigned to a student. The objective of this study was to find out a suitable method for its removal from aqueous solution. Literature survey revealed that most of the dyes are removed only by adsorption methods (Venkataraman 1952;

Deo Namita ,Ali Manzoor 1993) . The application of other potential separation techniques like Liquid-Liquid Extraction (LLE) is scarce. Hence LLE was considered as an alternative procedure. The application of such a separation technique gives the student a practical exposure to the theoretical concepts discussed in the classroom. A brief overview of LLE and its utility for the study is discussed below.

LIQUID-LIQUID EXTRACTION (LLE)

Liquid-Liquid Extraction is a technique, which involves the distribution of the solute between immiscible solvent. The Distribution Ratio (D) for the solute is given by the Nernst Distribution Law as

$$D = \frac{\text{Concentration of solute in organic layer}}{\text{Concentration of solute in aqueous layer}}$$

On a laboratory scale, solvent extraction is performed by mixing a known concentration of the solute with the extraction solvent in a separating funnel. After allowing sufficient equilibration time by agitation, the two phases (aqueous and organic) are separated. The concentration of the extracted species is found in both the layers by a suitable analytical technique.

An appropriate solvent for extraction is chosen based on the following criteria.

- *High distribution ratio:* The solvent employed must have an high distribution ratio for the desired solute and a low distribution for the undesirable impurities.
- *Low solubility in the aqueous phase:* The solvent must have low solubility in the aqueous phase.
- *Chemical stability and safety:* Solvent must be chemically stable and safe. It should not form any by-products that are explosive hazards.
- *Ease of recovery of the solvent:* The extracted solute has to be effectively removed by stripping on back extraction, in order to recover the solvent.
- *Low viscosity:* The solvent must have sufficiently low viscosity and appreciable density difference between the aqueous and organic phases to avoid the formation of emulsion.

Application Of LLE In The Removal Of Brilliant Green From Aqueous Solutions

The treatment of wastewater in chemical process industries is of paramount importance. The dyes present in wastewater are mostly removed by adsorption techniques. The commercial success of adsorption depends on the ease by which the loaded adsorbent could be regenerated.

LLE is an alternative separation technique and the regeneration technique is comparatively easier.

A number of dyes such as methyl violet, rhodamine, malachite green, brilliant green, etc., are present in the wastewater in the dye manufacturing units. These dyes are largely used for dyeing of silk wool, etc. Most of these dyes belong to the category of di or tri phenyl methane dyes.

Tri phenyl methane dyes.

Tri phenyl methane dyes are derived from the hydrocarbon triphenyl methane and the tertiary alcohol triphenyl carbinol (Chaudhuri Basab, et.al 1995).

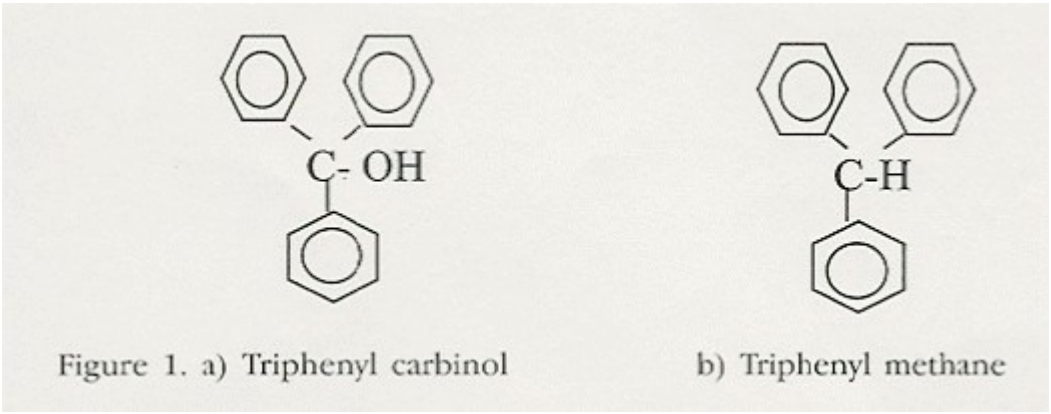

Figure 1. a) Triphenyl carbinol b) Triphenyl methane

Tri phenyl methane dyes may be divided into three groups. (1) malachite green series which contains two amino groups (2) Rosaniline dyes which contains three amino groups (3) Rosolic acid series which contain three hydroxyl groups . The amino or hydroxyl groups are in different benzene rings and para to the methane carbon atom. The structure of Brilliant Green is given below.

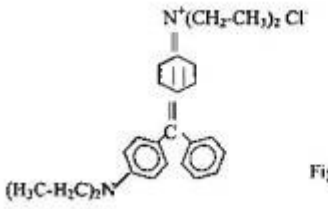

Figure 2. Brilliant Green

In dyeing, the oxalate or zinc chloride double salt is used. It gives pure green shade on wool and silk.

The study on the extraction of Brilliant Green was taken up as a project with the following objectives.

1. Selection of suitable solvent for extraction
2. Selection of a suitable stripping agent for the regeneration of the solvent.

The experimental procedure, the results and conclusions arrived at are discussed below.

Experimental

Instrumentation

A Spectronic- 20D UV-VIS spectrophotometer was used for measuring the absorbances.

Reagents

All reagents were of analar grade.

A stock solution of Brilliant Green was prepared by dissolving 0.01 gm in 100 ml of distilled water. 10 ml of this solution was diluted to 1000 ml. The λ_{max} of Brilliant Green was obtained by scanning the solution in the visible region. The λ_{max} was found to be 620 nm from the plot of absorbance against wavelength. A standard calibration graph for Brilliant Green solution was prepared with varying concentrations (ranging from 2-10 ppm). The absorbance was measured at 620 nm and a plot of absorbance versus concentration was linear in the above range, in adherence to Beer's Law.

Selection of Solvent

The solvent extraction was carried out by taking 10 ml of Brilliant Green solution of a known concentration and 10 ml of solvent in a separating funnel, and equilibrated for 10 minutes. The aqueous and organic layers were separated and collected. Extraction was done using three different solvents of varying polarities – Methyl Iso Butyl Ketone (MIBK), chloroform and toluene. Significant extraction was observed only with MIBK as the extractant. The concentration of Brilliant Green in the aqueous layer was found out by measuring the absorbance at 620 nm, by using the standard calibration graph. Since the aqueous layer was not completely decolorised after the first extraction, second extraction was performed by adding another 10 ml portion of the extractant.

Selection of a Suitable Stripping Agent

Triphenyl methane dyes can be reduced to their colorless leuco compounds. Reducing agents such as sodium sulphite and sodium nitrite were tried so as to strip the extracted Brilliant Green , thereby recovering the solvent. For the stripping of brilliant Green from the organic layer, the organic layer was equilibrated with 10 ml of sodium bisulphite solution. The retrograde extraction was continued with different portions of sodium sulphite solution, until the organic layer was decolorized completely. The results obtained are as follows.

Results and Discussion

The absorbances of the Brilliant Green solution before and after extraction into MIBK are given in Table 1. Since the aqueous layer was not completely decolorized by a single extraction for concentrations above 2 ppm, a second extraction was performed using 10 ml MIBK. The aqueous layer was completely decolorised after the second extraction. 10 ml of 10% sodium sulfite was added to the organic layer for re-extracting Brilliant Green. The results are summarized in Table 2. Varying concentrations of Na_2S0_3 were used for optimization. The results are presented in Table 3.

Conclusion

From the above results, it is clear that MIBK is a reasonably good solvent for the extraction of Brilliant Green. The extraction process might probably involve the solvation of Brilliant Green by MIBK, There is a considerable decrease in the absorbance of the organic layer with increasing concentrations of sodium sulfite. Using 25% of sodium sulfite, triple stripping had to be carried out to reduce the absorbance value considerably.

Further study could be carried out to study the feasibility of separation of a mixture of dyes by Liquid-Liquid extraction.

Initial Concentration (ppm)	Initial Absorbance of Brilliant Green solution	Absorbance of aqueous layer after first extraction
2	.335	.022
4	.624	.165
6	.915	.131
10	1.400	.049

Table 1. Single extraction of Brilliant Green solution using MIBK.

Con. Of Brilliant Green (ppm)	Organic layer after single stripping		Organic layer after second stripping		Organic layer after third stripping	
	Abs.	Con. (ppm)	Abs.	Con. (ppm)	Abs.	Con. (ppm)
4	.229	2.0	.133	1.1	.105	0.9
6	.300	2.6	.169	1.5	.140	1.2

Table 2. Stripping of organic layer using 10% sodium sulfite.

Con. of sod. Sulfite (%)	Organic layer before stripping		Organic layer after stripping					
	Abs.	Con. (ppm)	First stripping		Second stripping		Third stripping	
			Abs.	Con. (ppm)	Abs.	Con. (ppm)	Abs.	Con. (ppm)
10	.500	4.4	.229	2.0	.133	1.1	.105	.9
20	.582	5.1	.291	2.5	.164	1.4	.090	.7
25	.730	6.3	.298	2.6	.136	1.2	.073	.6

Table 3. Concentration of organic layer for varying concentrations of sodium sulfite.

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