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Removal and Recovery of malachite green and methyl violet dyes from textile wastewater using 2-nitrobenzoic acid as an extractant

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Abstract: Many industries use dyes extensively in different operations such as textile, paper, plastic, dyeing, pharmaceutical, and cosmetic, leather tanning etc., for coloring their final products. The release of coloured wastewater from these industries may present eco-toxic hazard and may eventually affect human through food chain. These colored compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. Some dyes are either toxic or mutagenic and carcinogenic. Thus, the removals of dyes from wastewater before they are mixed up with unpolluted natural water bodies are important. Various methods have been used to remove dyes from aqueous solutions. Liquid-liquid extraction (LLE) is significant potential to remove the dyes from wastewater. In the present study, we selected two different kinds of cationic dyes namely methyl violet and malachite green for liquid-liquid extraction using 2-nitrobenzoic acid in benzene as an extractant. The influencing parameters such as effect of extractant concentration, effect of diluents, effect of dye concentration, effect of pH and various stripping agents were investigated. The reusability studies were also conducted.

Keywords: Liquid-liquid Extraction; Methyl violet; Malachite green; Wastewater; Recovery.

Introduction

Dyes and pigments represent one of the problematic groups; they are emitted into wastewaters from various industrial branches, mainly from the dye manufacturing and textile finishing¹ and also from food coloring, cosmetic, paper and carpet industries to color the products. Textile and dyeing industry effluents can create serious environmental pollution problems when they are discharged into water bodies. The untreated effluents possess toxic with suspected carcinogenic and mutagenic effects that affect aquatic biota and humans. Synthetic dyes usually have complex aromatic molecular structures which make them more stable and these compounds have recalcitrant nature and their release into the environment poses serious environmental, esthetical and health problem and reduces the photosynthesis by decrease in oxygen penetration to water². Thus, the removal of dyes from wastewater before they are mixed up with unpolluted natural water bodies is important³.

Here we used two cationic dyes, such as methyl violet, malachite green. Methyl violet is chiefly used in copying papers, in heterograph and printing inks. It imparts deep violet colour in paints and printing inks. It is also used to obtain shades of deep colors that can be applied for the dyeing of cotton, silk, paper, bamboo, weed, straw and leather. It is toxic by releasing toxic substances when decomposed, such as CO, CO₂, NO, etc. For animals or human body, direct contact with methyl violet can cause pain and congestion while inhaling them could irritate the respiratory and gastrointestinal systems⁴. Malachite green (MG), a basic dye, is most widely used for coloring purpose. This triarylmethane dye is widely used in the aquaculture industry worldwide as a biocide as well as in the silk, wool, cotton, leather, paper and acrylic industries as a dye. However there are several reports describing its hazardous and carcinogenic effects. In humans, contact of malachite green with the skin causes irritation with redness and pain; upon contact with eye will lead to permanent injury of human eyes. It also affects the aquatic life and causes detrimental effects in liver, gill, kidney, intestine, gonads and pituitary gonadotrophic cells⁵. So it is important to adopt some treatment methods before discharging the effluents into water to reduce the harmful effects.

The methods employed for the removal of dyes from wastewaters include chemical oxidation⁶, reverse osmosis, ion exchange⁷, flocculation, adsorption on activated carbon⁸, and biological treatment. These methods are less efficient, expensive and produce wastes which are difficult to dispose and transfer the pollutants from one phase to other phase. The above mentioned methods are only removing the colors and not recovering the dyes from wastewater. In recent years, much attention has been focused on a separation technique such as solvent extraction or liquid – liquid extraction (LLE). Liquid-liquid extraction (LLE) is significant potential to remove the dyes from wastewater⁹. LLE is based on the principle that a solute can distribute itself in a certain ratio between immiscible solvents, and the extraction process depends on its mass transfer rate¹⁰. LLE offers significant advantages in toxicological analysis such as pre concentration of toxic substances, simplicity, low cost, compatibility with analytical systems. Muthuraman, et al.,¹¹ reported the extraction and recovery of methylene blue from industrial wastewater by LLE, using benzoic acid as the extractant. Similarly, golden yellow low salt anionic – type dye was extracted and recovered from aqueous solutions by the solvent extraction method was reported¹². Recovery of methylene blue from aqueous solution by liquid-liquid extraction was also reported¹³.

The objective of this work was to investigate the potential of 2-nitro benzoic acid with benzene as a novel extractant in the removal of the cationic dyes, methyl violet and malachite green, from aqueous solutions. The liquid-liquid extraction studies were carried out to investigate the effects of various parameters such as effect of pH, effect of carrier concentration, effect of dye concentration and effect of stripping agent. were also thoroughly studied and reported here.

Experimental

Materials

Benzene, 2-nitro benzoic acid, methyl violet, malachite green were obtained from Merck and used without further purification. The following acids and organic solvents such as methyl violet (99.8%), malachite green (99%), 2-nitro benzoic acid (95%), acetic acid (99%), oxalic acid (99%), sulphuric acid (98%), nitric acid (70%), hydrochloric acid (35.4%), benzene ($\geq 99\%$), toluene (98%), hexane (99%), xylene (99%) were used without further purification.

All chemicals used were analytical reagents grade and aqueous solutions were prepared in double distilled water.

Apparatus and measurements

A UV visible spectrophotometer (ElicoSI 159, India) was used to find out λ_{max} and measure dye concentration in the raffinate phase and strip solution. pH meter (Elico Li 120, India) was used to measure pH of aqueous solutions. For agitation of solution a shaker and stirrer was used (IKD-KS 50, India). Systronics Electrophoresis 606 was used to find out whether the dye is cationic or anionic.

Preparation of dye solutions

A stock solution of 1000 mg/L of MV and MG was prepared by dissolving an appropriate quantity of each dye which was diluted in a liter of deionized water. The working solutions were prepared by diluting the stock solution with deionized water to give the appropriate concentration of the working solutions.

Procedure

Liquid- liquid extraction

The extraction process was carried out by mixing an equal volume (10 mL) of aqueous solution of dye and organic solution of (benzene + 2- nitro benzoic acid) in a glass-stoppered bottle and the glass-stoppered bottle was shaken at 100 rpm for 5 min in a shaker. After equilibrium was established, the phases were separated using separating funnel. Sample of aqueous solution at the bottom of the separating funnel was taken for absorbance measurement of dye. The same procedure was carried out in each dye. The wavelength of maximum absorption (λ_{\max}) for MV and MG was 583 nm and 618 nm. The distribution ratio (D) and percentage of extraction (E) were calculated as per the following equations.

$$D = [\text{dye}]_{\text{org}} / [\text{dye}]_{\text{aq}} \quad (1)$$

$$E = 100 \times \{ [\text{dye}]_{\text{aq}0} - [\text{dye}]_{\text{aq}} \} / [\text{dye}]_{\text{aq}0} \quad (2)$$

Where $[\text{dye}]_{\text{org}}$: dye concentration in the organic phase (mg/L);

$[\text{dye}]_{\text{aq}0}$: initial dye concentration in the aqueous phase (mg/ L);

$[\text{dye}]_{\text{aq}}$: dye concentration of aqueous phase after extraction (mg/L)¹⁴.

In stripping process, the loaded extractant and the aqueous strippant (acid solution) were added together into a glass-stoppered bottle and shaken at 100 rpm for 5 min in a shaker. The content was then transferred into a separating funnel. The aqueous strippant was taken for dye concentration measurements. All the experiments were run in duplicate and analytical parameters were performed in triplicate for each run. Confidence limit of 98% was taken for reliable results.

Results and Discussion

Effect of pH in the feed phase

The pH of the extraction solution is considered one of the most important factors affecting the extraction process. In MV below pH 2 changed colour from dark violet to light violet and the original dark violet colour was changed above pH 11 whereas in MG below pH 2 changed colour from dark green to light green and the original dark green colour was disappeared in above pH 11. Hence the effect pH of solution was studied between 1.0 to 11.0 shown in Fig. 1. The extraction amount increased with increasing pH from 3 to 7. Thereafter increase in pH did not cause significant increase in extracted amount of dye. At pH 1 the extractant becomes positively charged, concentration of H^+ was high and they compete with MV and MG cations. So the percentage of dye extraction decreases. At the solution pH above 3, the extractant gets negatively charged and favours uptake of cationic dyes due to increased electrostatic force of attraction. At pH 7, the extractant was negatively charged to its maximum extent. Further increase in pH did not increase extraction capability. Therefore, pH 7 was used for extraction studies.

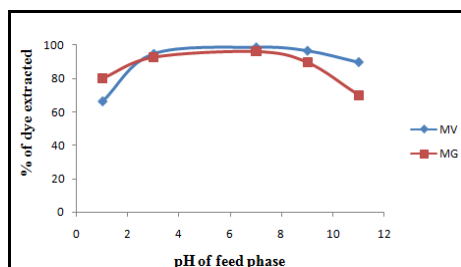


Fig.1. Effect of pH in the feed phase (Experimental conditions: Volume of feed phase = 10 mL, extractant concentration = 0.1 g, volume of organic phase= 10 mL,dye concentration = 20 mg/L, stripping agent concentration = 10 M).

3.2. Effect of extractant concentration

Extractant concentration is an important parameter because it determines the capacity of an extractant for a given initial concentration of dye. The effect of extractant concentration was studied with MV and MG dye removal keeping all the experimental conditions constant. The extraction of dyes by 2-nitro benzoic acid at different extractant concentrations from 0.05 g. to 0.5.g. for 20 mg/L of dye concentration at pH 7.0 was studied. The results are shown in Fig. 2. The result (Fig. 2.) shows that as the extraction concentration increases

from 0.09 to 0.1 g., the percentage of extraction of dyes increases. Further increase in extractant concentration, did not show significant increase in% removal of dye, therefore, 0.1 g of extractant was chosen for the successive experiments.

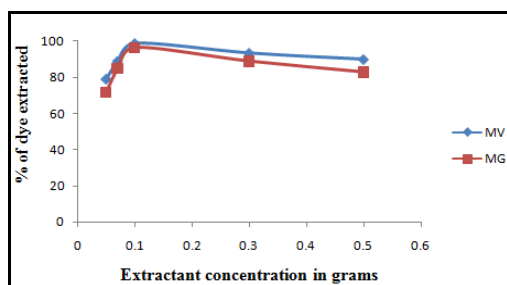


Fig.2. Effect of extractant concentration (Experimental conditions: Volume of feed phase = 10 mL at pH 7.0 ± 0.1 , volume of organic phase = 10 mL, dye concentration = 20 mg/L, stripping agent concentration = 10 M).

3.3. Effect of initial dye concentration

The effect of dye concentration on the extraction process was tested at fixed extractant concentration. The extraction percentage of various initial concentrations of cationic dyes in the range 20 mg/L to 100 mg/L was studied and the results are shown in Fig. 3. At initial dye concentration of 20 mg/L, 98.95% of extraction was obtained. Further increase the initial dye concentration in the aqueous phase, the percentage of extraction decreases. Because, in higher concentration of dye has higher energy, and high in color. So, the extractant cannot able to extract the dye completely. Hence, the subsequent extraction studies were conducted using 20 mg/L of dye concentration.

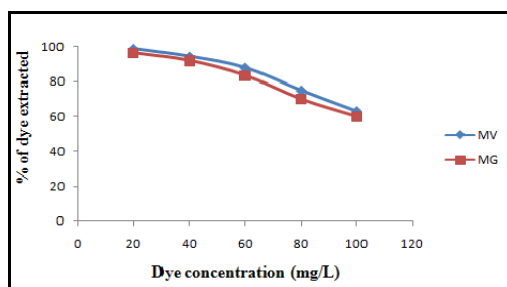


Fig.3. Effect of dye concentration (Experimental conditions: Volume of feed phase= 10 mL, volume of organic phase = 10 mL,pH 7.0 ± 0.1 , extractant concentration = 0.1g, stripping agent concentration = 10 M).

3.4. Effect of stripping reagents

In any extraction processes, it is very imperative to back extract the extracted dye from the organic phase. Here sulphuric acid, nitric acid, hydrochloric acid, oxalic acid, acetic acid, sodium hydroxide, sodium carbonate, sodium bicarbonate, potassium hydroxide have been tried as stripping agents. Among them acetic acid was best to strip the dye from loaded organic phase. Other stripping agents changed the dye colour and not striped the dye. Further studies were carried out using acetic acid as stripping agent. Table.1 shows the stripping efficiency increased with increasing concentration of acetic acid from 7 M to 10 M. Maximum stripping efficiency of 98% was obtained at 10 M of acetic acid. Further increase the acetic acid concentration did not improve stripping efficiency. Hence, further studies were carried out using 10 M acetic acid as stripping agent.

Table 1 Effect of stripping agent concentration

Stripping agent concentration	Percentage of stripping (%)
3 M acetic acid	69
5 M acetic acid	80
7 M acetic acid	95
10 M acetic acid	98

Conclusion

The following conclusions can be drawn based on the investigation of MV and MG dye extraction by 2-nitro benzoic acid with benzene as extractant. The percentage extraction of dyes increased with increasing extractant concentration and decreased with increase in initial concentration of dye solution. Higher percentage of extraction (98.95%) of dyes was observed at pH 7. 10 M acetic acid stripped the dye very well and stripped dye and extractant reused again up to 10 cycles very effectively. These reused studies reduced the pollution of the environment.

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