



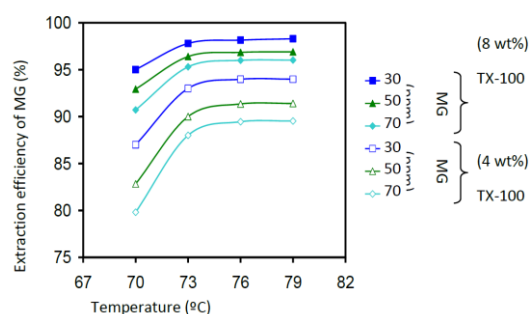
CLOUD POINT EXTRACTION OF MALACHITE GREEN DYE FROM WATER SAMPLES USING TRITON X-100 AS NONIONIC SURFACTANT

Moussa ALIBRAHIM*

Department of Chemistry, Atomic Energy Commission, P.O. Box 6091, Damascus, Syrian Arab Republic

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A surfactant-based cloud point extraction (CPE) was developed to remove color from wastewater containing malachite green (MG), using TritonX-100 (TX-100) as a nonionic surfactant. Most of the dye molecules are solubilized in the coacervate phase, leaving a dilute phase free of dye. The effects of surfactant concentration, temperature and salt concentration on different dye concentrations were studied and optimum conditions were obtained for MG removal. The MG concentration in the diluted phase was measured using a UV-Vis spectrophotometer. It was found that the phase separation was complete and the MG recovery was highly efficient in the presence of NaCl as the electrolyte. The results showed that up to 70 ppm of MG, more than 95% can be quantitatively removed by the CPE procedure in a single extraction under optimum conditions. It is concluded that the cloud point extraction techniques for the dye removal may be an alternative to the present dye removal processes.



INTRODUCTION

Many industries, such as dyestuffs, textile, paper and plastics, use dyes in order to color their products and consume substantial volumes of water. As a result, they generate a considerable amount of colored wastewater. It is recognized that public perception of water quality is greatly influenced by the color.^{1–3} The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable. Due to their good solubility, synthetic dyes are common water pollutants and are frequently found in trace amounts in industrial wastewater.⁴ Malachite Green (MG) is widely used in textile, ink, paint, paper and leather industries.⁵ The

effluent containing MG is green in color and toxic. The strong color of the dye causes considerable damage to aquatic life. MG does not allow sunlight to pass through and thus affects the photosynthesis of aquatic plants.⁶

Many investigators have studied different techniques for removal of colored dye from wastewater, *e.g.*, micellar enhanced ultrafiltration (MEUF),⁷ various advanced oxidation processes,^{8,9} ozonations,^{10,11} nanofiltration^{12–14} and adsorption on to (i) sludge of wastewater treatment plant¹⁵ (ii) different bentonites¹⁶ and (iii) various types of activated carbon,^{17–21} etc. Ultrafiltration (UF) and nanofiltration (NF) can be used to completely remove all classes of dyes, but care must be taken to avoid membrane fouling that reduces flux. Due

* Corresponding author: cscientific25@aec.org.sy

to the low biodegradability of dyes, a conventional biological wastewater treatment process is not very effective in treating wastewater containing dyes.²² Physical or chemical treatment processes are typically used to treat them.²³ Adsorption is a common treatment process. Previous investigators have studied the adsorption of dyestuffs using a variety of natural adsorbents, but yet these adsorbents are impractical for the effluent of modern textile industries. Activated carbon can effectively be used to remove color although it is ineffective for dispersed dye.²⁴

In the last decade, increasing interest on the use of aqueous micellar solution has been found in the field of separation science.²⁵ At a certain temperature, the aqueous solution of a nonionic surfactant becomes cloudy. When the temperature increases further, the solution separates into two phases: one is a surfactant-rich phase, which has a small volume relative to the solution and is called the coacervate phase, and the other is a bulk aqueous solution containing a surfactant concentration slightly higher than the critical micelle concentration (CMC).²⁶ This temperature is known as cloud point temperature (CPT) of the surfactant. The solute present in the aqueous solution of the nonionic surfactant is partitioned between the two phases at the cloud point temperature.²⁷ This phenomenon is known as cloud point extraction (CPE).

In this work, we adopted the cloud point extraction technique for the removal of MG from wastewater using TritonX-100 as nonionic surfactant. The effects of temperature, surfactant, dye and salt concentrations on dye extraction were studied. The cloud point curve of TX-100 in water was accurately and authentically determined to determine the temperature required for MG extraction. The novelty of the work is the extraction of different concentrations of MG from aqueous media using specific concentrations of TX-100 at temperatures ranging from 70°C to 79°C, at which phase separation occurred without any salt additions, with good results. Based on these results related to MG extraction under these conditions, the extraction efficiency was then improved by adding sodium chloride, and the optimum temperature at 79°C was determined. In addition, the fractional coacervate phase volumes were accurately and authentically determined at different temperatures and specific concentrations of TX-10 and MG, which is important for determining extraction efficiency due to the accumulation of micelles in it, especially as the temperature increases from 70°C to 79°C.

EXPERIMENTAL

Materials

The dye used in this study is Malachite Green (MG) (molecular weight: 927.00, λ_{\max} : 617 nm, supplied by Sigma, USA). TritonX-100 (iso-octyl phenoxy polyethoxy ethanol) containing approximately 10 ethoxy units per molecule (molecular weight: 628, λ_{\max} : 226 nm), supplied by Avonchem, UK, was used as the nonionic surfactant. The electrolyte used is sodium chloride (purchased from Prolabo, EEC). All the chemicals were used as received without further purification. Doubly distilled water was used to prepare sample solutions.

Methods

The cloud point temperatures (CPT_s) of surfactant solutions were determined visually point by point by preparing aqueous solutions containing from 0.10 to 30 wt % surfactant. Aliquots (1–2) cm³ were enclosed in small capped vials immersed in a thermostated bath. The temperature was progressively raised until the solution became turbid. The uncertainty range could be decreased up to $\pm 0.1^\circ\text{C}$. The temperature at which the turbidity disappeared upon cooling was also noted. The cloud point temperatures (CPT_s) presented in this paper are averages of the cloud appearance and disappearance temperatures. These temperatures did not differ by more than 0.4°C. The (CPE) process could only take place at a temperature higher than the (CPT_s) of nonionic micellar solutions.

In the CPE experiments, solution (50 ml) of TX-100 and Malachite Green (MG) has been prepared by dissolving accurately weighed amount of surfactant and dye, respectively, in distilled water at different concentrations. The concentrations of dye in feed are 10, 30, 50, 70 and 90 ppm. The concentrations of TX-100 in feed are 4, 6, 8 and 10 wt %. To observe the effect of salt on the CPE of the dye, the salt concentration (NaCl) was selected as 0.0025, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05 and 0.06 M. Each experiment was carried out using a 50 mL graduated cylinder containing different concentrations of dye, TX-100 and salt solution in a constant temperature bath for 30 min.

After complete phase separation, measuring cylinder is removed from the temperature bath and cooled for 3 min. The coacervate phase volume and concentration of dilute phase have been measured. All the experiments have been conducted at four different temperatures (70°C, 73°C, 76°C and 79°C). The concentration of dye has been determined by spectrophotometer (make: Hach, Belgium; model:

DR/3000 spectrophotometer). Pure (MG) solution is initially calibrated for different concentrations in term of absorbance units, which is recorded at the wavelength of 617 nm, at which maximum absorption takes place.

For cloud point extraction, the extraction efficiency is defined as follows:

$$\text{Efficiency of extraction} = \left(1 - \frac{C_d}{C_0}\right) \times 100$$

where C_0 and C_d are the initial and dilute phase concentration of (MG) respectively. The effects of various operating conditions on the degree of dye separation were studied and the optimum concentrations were established for CPE.

RESULTS AND DISCUSSION

Cloud point temperature as a function of surfactant concentration

The dependence of cloud point temperature of TritonX-100 on its concentration in water is

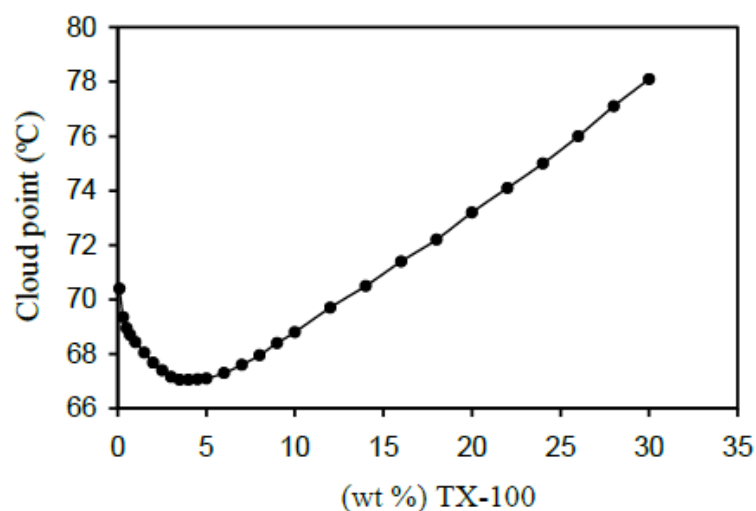


Fig. 1 – Cloud point of TX-100 as a function of (wt %) of TX-100 in solution.

Cloud point extraction

Effect of surfactant and dye concentration

For successful CPE of the dye, it is desirable to use a minimum amount of surfactant for maximum dye extraction. Figures 2 and 3 show the effects of TX-100 concentration on MG extraction from different initial concentrations at 70 °C and 79 °C, respectively. It has been observed from both figures

illustrated in Fig. 1. It shows a peak on the curve of cloud point as a function of TritonX-100 concentration. With increasing TritonX-100 concentration, the CP decreases in the dilute regime and then increases after reaching a minimum value. The concentration at which the cloud point is lowest is 3.75 wt % and the corresponding temperature is 67.1°C. A similar trend on the change in cloud point temperature with increasing surfactant concentration in dilute regimes has been reported elsewhere for some other surfactants.^{28,29} Below the cloud point curve, there is only one liquid phase (micellar phase), whereas two coexisting liquid phases, the surfactant rich micellar phase and water phase, are found in the region above the curve. TritonX-100 represents typical clouding behavior of nonionic polyethoxylated surfactant.^{30–32} Notably, this nonionic surfactant is commercial blends and mixtures, so that it is quite common to find temperature deviation of the cloud point curve from surfactant manufactured in different batches.

that for MG concentrations of 10, 30, 50, 70 and 90 ppm, extraction of MG increases sharply when TX-100 concentration increases 4-8 wt %. Beyond 8 wt %, the increase in extraction efficiency becomes gradual. For a MG concentration of 10 ppm, 100% MG extraction is possible with a TX-100 concentration of 10 wt %. For 10, 30, 50, 70 and 90 ppm of MG concentration, 8 wt % TX-100 may be an optimum concentration to achieve about (90–99) percent extraction of MG.

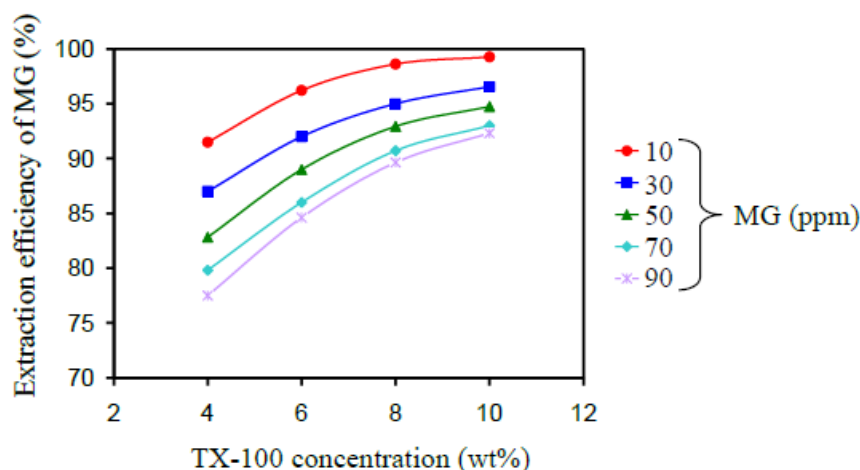


Fig. 2 – Effect of feed *concentrations* of TX-100 and MG on the extraction efficiency of MG at 70°C.

It may be observed from Fig. 3 that at a fixed temperature and feed MG concentration, the MG extraction efficiency increases with the feed TX-100 concentration. The concentration of the micelles increases with the feed TX-100 concentration, resulting in greater solubilization of MG in the micelles. Since the surfactant concentration in the dilute phase remains around the CMC,²⁶ the surfactant micelle concentration (along with the solubilized dye) in the coacervate phase increases to maintain material equilibrium. Therefore, the dye extraction efficiency increases with the feed

surfactant concentration. From Figs. 2 and 3, it may also be observed that the MG extraction efficiency decreases with the feed MG concentration. At a particular operating temperature and surfactant concentration, the surfactant concentration in both the dilute and coacervate phase remains constant. Hence, the dye solubilization capacity of surfactant micelles remains almost invariant in the coacervate phase. Therefore, with the further increase in feed dye concentration, excess dye remains unsolubilized in the dilute phase, resulting in a decrease in dye extraction efficiency.

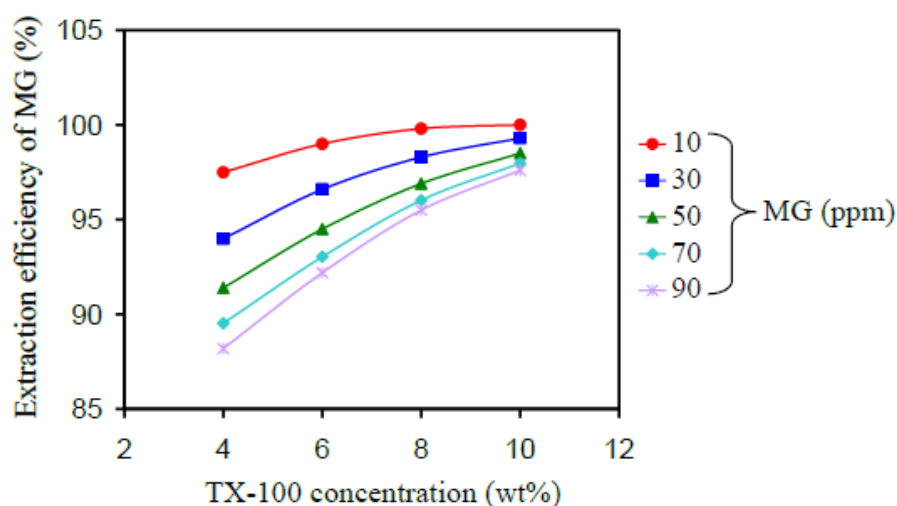


Fig. 3 – Effect of feed concentrations of TX-100 and MG on the extraction efficiency of MG at 79°C.

Effect of temperature

The effects of operating temperature on MG dye extraction efficiency are also evident in Figs. 2 and 3. The MG extraction efficiency increases with

temperature. For example, extraction efficiency of MG solution at 50 ppm, is about 82.82% at 4 wt % TX-100 concentration at 70 °C (Fig. 2); whereas it is about 91.40% at the same concentration level at 79 °C (Fig. 3). At TX-100 concentration of 10 wt %, the

extraction efficiency of all the MG concentrations used in the present study increases from 92.32% to 99.27% (Fig. 2) to about 97.60–100% (Fig. 3), when temperature increases from 70 to 79°C.

Figure 4 shows also the effect of temperature on the efficiency of CPE for the initial MG concentrations of 30, 50 and 70 ppm, respectively, using 4 and 8 wt % of TX-100. It is clear from the figure that the extraction of MG increases with increasing temperature and concentration of feed TX-100. It can be observed that the extraction of MG (for 30 ppm feed MG and 8 wt % TX-100) increases from 95.01–98.30% as the temperature increases from 70 to 79°C. The increase in extraction or solubilization efficiency of dyes in micelles with increasing temperature may be due to the fact that the polarity of the MG molecule decreases with increasing temperature and shows a preferentially hydrophobic nature at higher

temperature. Therefore, MG molecules solubilize in micelles. A similar trend is observed for higher MG feed concentration, but the extraction efficiency decreases with increasing MG feed concentration. As the temperature increases, the following three phenomena can occur simultaneously, (i) the number of micellar aggregations increases due to increased hydrophobicity,^{33,34} (ii) the repulsive micellar interaction forces become attractive,^{34,35} (iii) dehydration occurs in the external ethoxy groups of the surfactant and water becomes a poor solvent for the surfactant molecules.^{34,36} This improves the phase separation and increases the micellar concentration in the coacervate phase, resulting in greater solubilization of the dye molecules. This directly leads to an increase in the dye extraction efficiency with temperature.

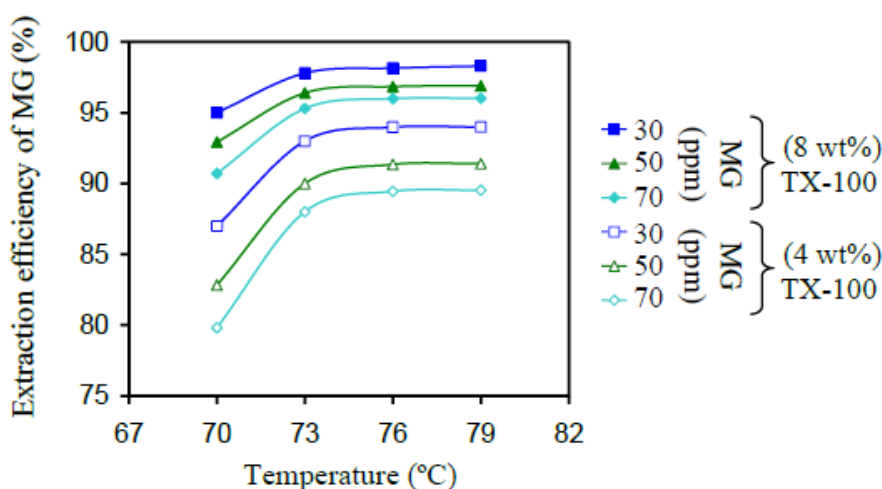


Fig. 4 – Effect of temperature on the extraction efficiency of MG for 30, 50 and 70 ppm of MG at TX-100 concentration of 4 and 8 wt%.

In general, the results of the effects of operating temperature on MG extraction efficiency indicated that MG extraction increases with temperature at different MG concentrations up to a temperature of 79°C and is constant above this temperature. Thus, the temperature of 79°C has been used in other studies.

Variation of the coacervate phase volume

The fractional coacervate phase volume variation with temperature for two TX-100 feed concentrations and various MG feed concentrations is shown in Fig. 5(a, b). It can be observed from this figure that the volume of the coacervate phase decreases with temperature. For

example, at 30 ppm MG and 8 wt % TX-100, the fractional volume of the coacervate phase decreases from 0.580 to 0.225 as the temperature is increased from 70 to 79°C. As previously noted, at elevated temperature, the interaction between TX-100 micelles increases, leading to dehydration of the outer layers of the micelles resulting in a decrease in the volume of the coacervate phase. Furthermore, as can be seen from the figure, the volume of the coacervate phase is larger for higher TX-100 feed concentration. This is simply because there will be more surfactant micelles in the coacervate phase after phase separation and thus will increase the volume of the coacervate phase. It is also evident from Fig. 5(a, b) that the volume of

the coacervate phase increases with the dye concentration at constant temperature and surfactant concentration. For example, at a temperature of 73°C and 8 wt % TX-100, the fractional volume of the coacervate phase increases

from 0.348 to 0.375 as the MG concentration increases from 30 to 70 ppm. This is because as the dye concentration increases, more dye will be solubilized, which will result in an increase in the fractional volume of the coacervate phase.

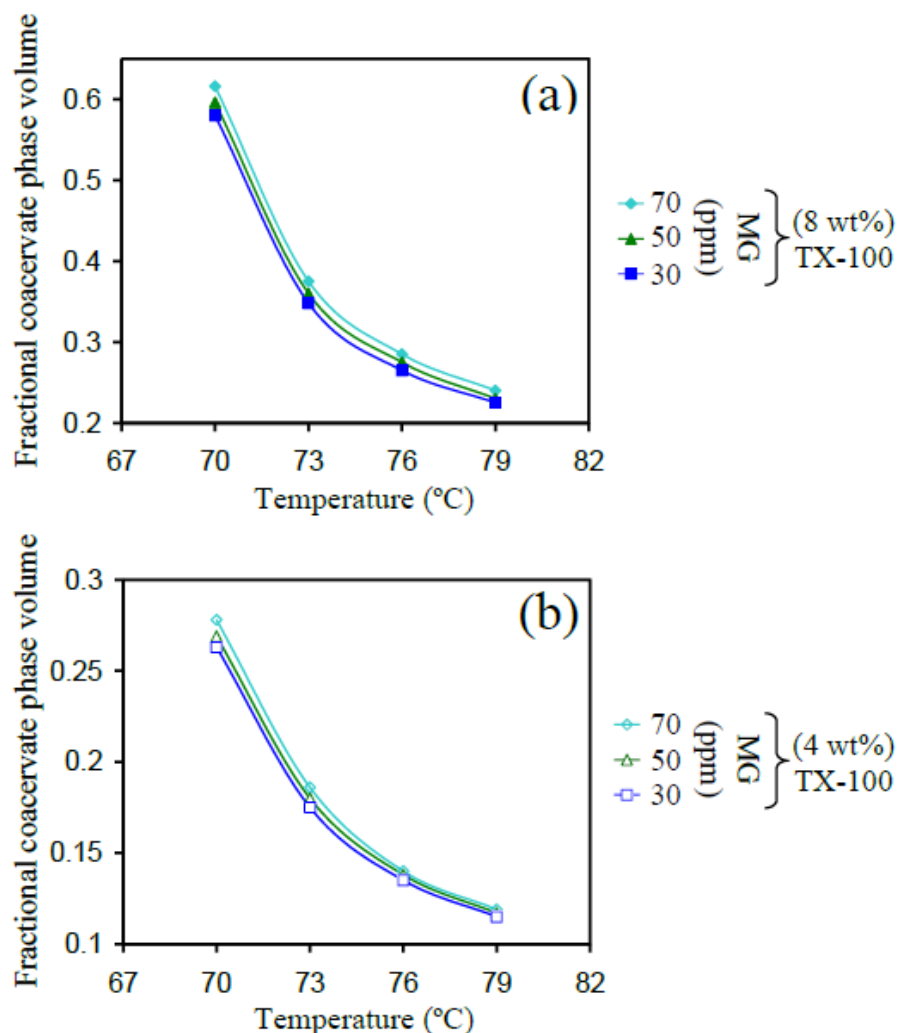


Fig. 5(a, b) – Effect of temperature on the fractional coacervate phase volume at different feed MG and TX-100 concentrations.

Effect of salt concentration (salting out)

Figures 6 and 7 show the variation of extraction efficiency with NaCl concentrations at TX-100 concentration of 0.064 M and at 79°C for initial MG concentrations of 50 and 70 ppm, respectively. It can be observed from both figures that the MG extraction efficiency increases with NaCl concentration. From Figure 6, it is observed that the MG extraction increases sharply from 91.40 to 92.90% up to 0.02 M NaCl, but beyond that, the increase in efficiency becomes gradual. It is well known that due to its salting out effect, sodium chloride decreases the CPT of the surfactant and

promotes the dehydration of ethoxy groups on the outer surface of the micelles.³⁴ Therefore, the addition of NaCl increases the phase separation, improving the micellar concentration in the coacervate phase as well as the concentration of solubilized dyes. Therefore, the dye extraction efficiency increases with the salt concentration. The volume of the fractional coacervate phase decreases with the salt concentration. Due to the salting out effect, more water passes into the dilute phase, decreasing the volume of the coacervate phase. A similar trend is observed in Fig. 7 for higher MG concentration.

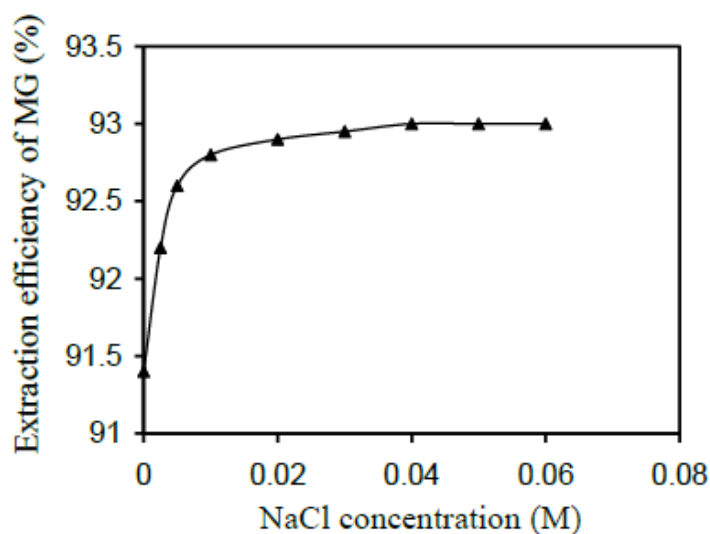


Fig. 6 – Effect of NaCl concentration on the extraction efficiency of MG (50 ppm) in the presence of (0.064 M) TX-100 at 79 °C.

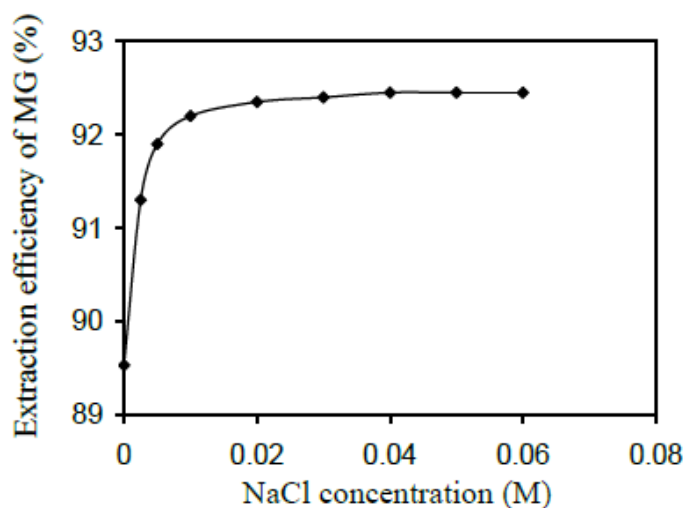


Fig. 7 – Effect of NaCl concentration on the extraction efficiency of MG (70 ppm) in the presence of (0.064 M) TX-100 at 79 °C.

CONCLUSION

Cloud point extraction was successfully applied to remove Malachite Green (MG) from wastewater using TX-100 as nonionic surfactant. The extraction efficiency increased with temperature, TX-100 and NaCl concentrations. From the experimental results, it was observed that for dye concentration of 10 ppm, 100 % removal of Malachite Green dye is possible with TX-100 concentration of 10 wt %. For higher dye concentration up to 90 ppm, 96–99 % removal of dye can be achieved using 0.127 M TX-100 and 0.02 M salt (NaCl) concentration at 79°C.

Future research will be conducted on the use of other surfactants, their application in cloud point

extraction processes for MG and other organic compounds, particularly polycyclic aromatic hydrocarbons (PAHS). The research will be expanded to include the application of salting-out technology using various inorganic salts, based on established scientific principles based on previously published research we have conducted. Future work aims to establish a semi-industrial unit for the continuous purification of industrial water contaminated with toxic PAHs.

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