

First Libyan international Conference on Engineering Sciences & Applications (FLICESA_LA)
13 – 15 March 2023, Tripoli – Libya

Investigation of Using Polyethylene Glycol-400 (PEG-400) As a Surfactant for Separation of organic dyes and some heavy metals from Water Samples by Cloud Point Extraction

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Abstract— Phase separation by cloud point phenomena depending strongly on the behavior of the surfactant used. This study aimed to apply a new surfactant for the separation of some toxic pollutants from water samples using cloud point extraction (CPE) methodology. Polyethylene glycol-400 (PEG-400) was chosen as surfactant to facilitate phase separation of Cr(VI), Cu(II), Fe(II), methyl green and methylene blue dye ions from water samples. The effect of some parameters on extraction percent, pH, surfactant amount, pollutant ions concentration, and temperature have been studied and optimized. As a result, PEG-400 is an excellent surfactant with satisfactory results since more than 95% of extraction percent has been reached.

Keywords— Cloud point extraction, Non-ionic surfactant, Pollution

I. INTRODUCTION

Pollution caused by higher levels of heavy metal ions and organic dyes in the environment due to technological and industrial development is one of the most important risks facing the world today. These pollutants in water bodies at certain concentrations that pose a threat to the ecosystem [1]. Most of these contaminants cannot biodegrade or detoxify easily and have a high tendency to accumulate, especially in living matter [2, 3]. Therefore, discharge of these pollutants into water recourses affecting water quality and causing harm to aquatic organisms due to its high toxicity, which makes it unsuitable even for human consumption.

The widely used of heavy metals and dyes in many industrial activities related to the manufacture of medicines, food and other commercial products such as cement industry, leather tanning, electroplating, production of refractory steel, catalytic manufacture, photographic material, corrosive paints and rubber manufacturing industries has contributed to a significant increase in their concentrations in the environment.

Therefore, the determination of these pollutants in aqueous and biological matrices is a very important tool for environmental and toxicological monitoring. Accordingly, it is very difficult because of the presence of these contaminants at low levels, which requires sensitive automated techniques and frequently a pre-concentration step such as liquid–liquid extraction (LLE), solid phase extraction (SPE), ion exchange, co-precipitation, and cloud point extraction (CPE).

Traditional liquid–liquid extraction and other mentioned methods have many disadvantages during the separation process, among of these, time-consuming, labor intensive and consume large amounts of high purity solvents, which are frequently toxic [4, 5]. In this sense, most industries are looking for alternative technologies that are competitive and can overcome some of the defects in the mentioned methods. As such, CPE is a new environmental-friendly method that has gained a significant interest in separation science.

In recent years, CPE, is considered an alternative approach for extraction, and pre-concentration technique, was successfully used in the separation of pollutants from environmental samples which reduces solvent consumption and extraction time and also provides high enrichment factors for analyses [6, 7]. The CPE mechanism is a very simple which involves forming hydrophobic species by solubilization of the pollutants in a medium containing surfactant. Then the hydrophobic complex is extracted after being incorporated into a micelle system when being clouding.

Separation by cloud point phenomena is mainly dependence on the phase behavior of non-ionic surfactants in aqueous media. Most non-ionic surfactants in aqueous media form micelles and become more turbid when heated to the cloud point temperature (CPT) or in the presence of a salting-out agent. Above the CPT, the surfactant solution is easily

separated into two immiscible phases as a result of the formation of micelles, a small volume of surfactant-rich phase containing the required solute with a small amount of water and a diluted aqueous phase which represents the rest of solution in which the concentration of the non-ionic surfactant is at equal, or below to, its critical micelle concentration (CMC) system [8-12]. Thus, in the present study, the extraction of ions from the initial aqueous solution was achieved by concentrating these ions into the surfactant-rich phase after formation of a hydrophobic complex.

According to some previous studies; removal of different pollutants, like heavy metals and/or organic dyes from aqueous solutions using CPE is an increasing interest in the scientific community. However, most recent investigations have focused on the use of low-cost surfactants with or without appropriate reagent [13-23].

Recently, in our research group, Asweisi et al. extraction of some metal ions using PO/EO block polymer as a surfactant with APDC was studied with satisfactory results [24]. In 2022, this study extended to use different surfactants, commercial polyethylene glycol, glycerine, PO/EO block polymer, and ethoxylated polyamine with APDC as cleating agent for extraction of cadmium ions from aqueous medium, as a result these surfactants had a good ability of extraction with high efficiency [25].

In this study, CPE method developed for the pre-concentration of Cr(VI), Cu(II), Fe(II), methyl green and methylene blue dye ions in various samples using PEG-400 as a surfactant because of their low cloud point temperature and high density of the surfactant-rich phase as well as their low cost, commercial availability and lower toxicity. Some parameters that effect on the extraction percent like sample pH, amount of surfactant, temperature, and concentration of pollutants have been investigated and optimized.

II. EXPERIMENTAL METHOD

A. Reagents

All solution samples were prepared with deionized and high purity water. Except if otherwise stated. Analytical-grade acids, methanol, and other chemicals used in this study are obtained from Merck, Darmstadt, Germany. The standard solution method was used to establish the calibration curve. A 1.0% (w/v) of PEG-400 surfactant was used.

B. Apparatus

A thermostated water bath, maintained at the desired temperature where the separation was achieved. The CPE measurements were made using UV-VIS spectrophotometer JENWAY with 20 mm quartz cells was used. The pH measurement was made by JENWAY 3150 PH-METER.

C. CPE procedure

A CPE experiments were prepared according to literature (Asweisi et al., 2020). Aliquots of 9 mL of the sample or standard solution containing, contaminated sample (7 mL), surfactant (2 mL), were heated in a thermostated water bath at 80 °C for 10 min. Separation of the diluted aqueous and surfactant-rich phase was achieved when the surfactant-rich phase became more viscous and immiscible. The aqueous phase was then easily separated completely by a 10 mL syringe centered in the tube and introduced into the UV-VIS

spectrophotometer JENWAY by the 20 mm quartz cells for analysis.

D. Analytical procedures

The experimental study of the separation process using cloud point phenomena was evaluated by the extraction yield percent (Equation 1), which is estimated from mass balance based on initial and final ions concentrations in the original solution before and after heating to CPT:

$$\%E = \left(\frac{C_0 - C_t}{C_0} \right) 100 \quad (1)$$

Where %E represents the percent of extraction of pollutant from an aqueous solution; C_0 and C_t are the initial and final concentration of pollutant ions in the aqueous phase, before and after extraction, respectively.

III. RESULTS AND DISCUSSION

Separation of some toxic metal ions such as hexavalent chromium studied under different experimental conditions. The change in extraction percent with pH shown in figure 1, more than 95% extraction at pH values between (9 and10), then the extraction percent decreased gradually with increasing pH values. Formation of stable metal hydroxides at higher pH values may occurred leads to less extraction possibilities of metal ions.

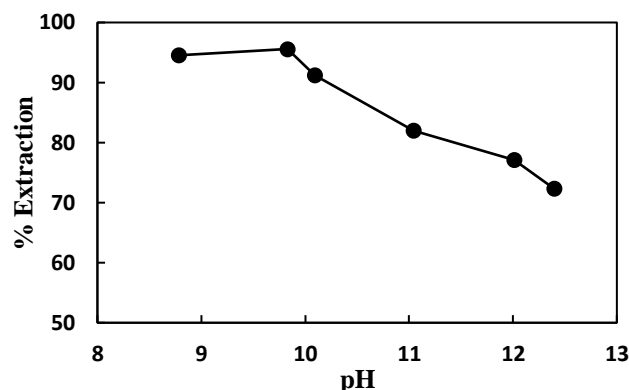


Fig. 1. Effect of PH on extraction percent of Cr (VI)

Separation of metal ions from aqueous solution to surface of surface-active materials by adsorption on liquid surface affected by the initial concentration of the metal ions. As can be seen from the figure below, the extraction percent increased with increased concentration of the metal ions up to 0.0015M, then it became lower at higher concentrations more than this value. This may be attributed to the saturation of the surfactant active sites.

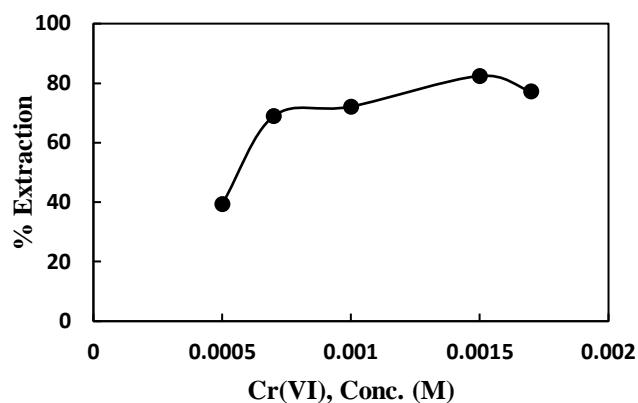


Fig. 2. Effect of concentration of Cr (VI) on extraction percent

Investigation of volumetric ratio of PEG-400 to the metal ion concentration is studied. Copper ions with different ratios showed different separation percent's. The optimum value of volumetric ratio of copper to surfactant is at 1:1 ratio. The results are shown in figure 3.

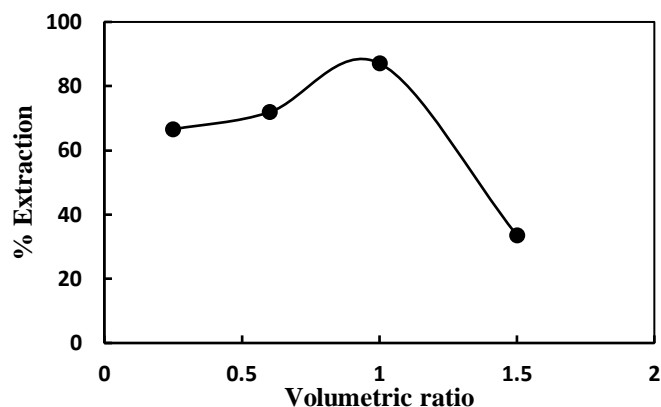


Fig. 3. The effect of volumetric percent of Cu (II) to PEG-400

In the case of Iron, Fe(II), the optimum volumetric ratio between Fe(II) and PEG-400 is found to be 0.75 at which about 90% separation of the metal reached as shown in figure 4.

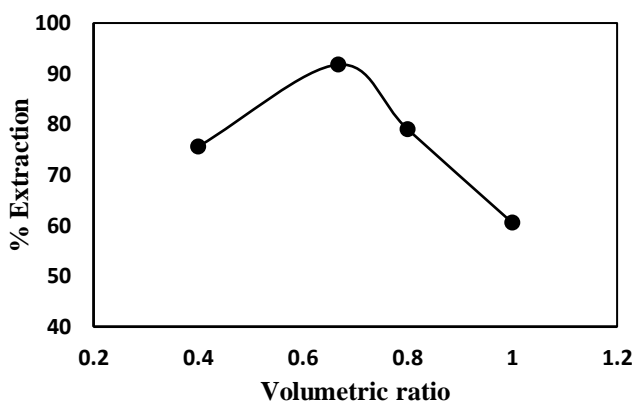


Fig. 4. Effect of volumetric ratios of Cu (II): PEG-400 on separation percent

The results of extraction of organic dyes (methyl green as an example) are shown in figure 5. The extraction percent is increased first with increasing of dye concentration up-to

0.00005M then the percent extraction decreased gradually with increasing dye concentration. The best conditions for separation are found to be 0.00005M of dye at a volume of 3.0mL surfactant and pH of 12.0.

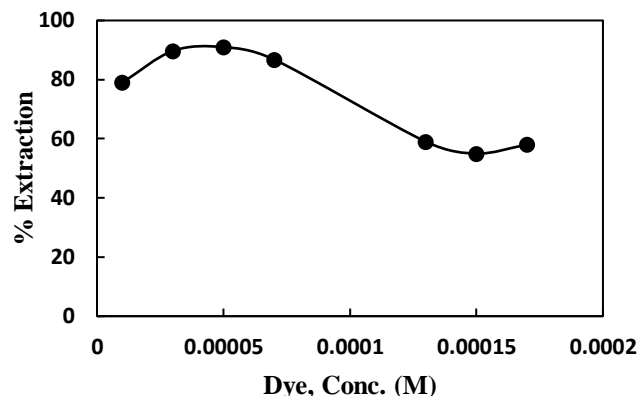


Fig. 5. Effect of concentration of M-green on extraction percent

IV. CONCLUSION

From the results obtained on can conclude that surface-active material PEG-400 could be used in separation and extraction of hexavalent chromium with more than 95% in one extraction step with a very small volume of surfactant. In addition, PEG-400 extracts other metal ions like copper and iron. PEG-400 works very well in the separation of organic dyes like methyl green and methylene blue as well as the proposed method has shown to be a very simple procedure, efficient, inexpensive, green and safe method.

ACKNOWLEDGMENT

We are gratefully acknowledgements to Chemical Eng. Department, University of Tripoli.

REFERENCES

- [1] R. Sivaranjane, P. Kumar, and S. Mahalaxmi, "A review on agro-based materials on the separation of environmental pollutants from water system," *Chem. Eng. Res. Des.*, vol. 181, pp. 423-457, May 2022.
- [2] A. Aswesi, and K. Algheryani, "Mechanism and Kinetic Studies of Methylene Blue Adsorption on Commercial Polyurethane Foam," *Journal of Alasmarya University: Basic and Applied Sciences*, vol. 6, pp. 714-724, December 2021 [Special Issue for 4th Conf. on Engineering Science and Technology (CEST-2021)].
- [3] J. Briffa, E. Sinagra, and R. Blundell, "Heavy metal pollution in the environment and their toxicological effects on humans," *Heliyon*, vol. 6, September 2020.
- [4] W. Mortada, "Recent developments and applications of cloud point extraction: A critical review," *Microchemical Journal*, vol. 157, September 2020.
- [5] K. Kiran, K. Kumarb, B. Prasad, K. Suvadhan, L. Babu, and K. Janardhanam, "Speciation determination of chromium(III) and (VI) using preconcentration cloud point extraction with flame atomic absorption spectrometry (FAAS)," *Journal of Hazardous Materials*, vol. 150, pp. 582-586, 2008.
- [6] Z. Sefrou, and N. Belkhouche, "Cloud point extraction of La(III) by C13E10 non-ionic surfactant: Statistical refinement of experimental optimization by L9 Taguchi's design," *Chem. Eng. Res. Des.*, vol. 153, pp. 819-828, January 2020.
- [7] Y. Yamini, and M. Ghambarian, "Environmental Applications of Cloud-Point Extraction," *Chemistry*, *Molecular Sciences and Chemical Engineering*, vol. 3, pp. 657-680, 2012.
- [8] H. Rezende, C. Nascentes, and N. Coelho, "Cloud point extraction for determination of cadmium in soft drinks by thermospray flame furnace

- atomic absorption spectrometry," *Microchemical Journal*, vol. 97, pp. 118–121, 2011.
- [9] L. Zhao, S. Zhonga, K. Fanga, Z. Qiana, and J. Chen, "Determination of cadmium (II), cobalt(II), nickel(II), lead(II), zinc(II), and copper(II) in water samples using dual-cloud point extraction and inductively coupled plasma emission spectrometry," *Journal of Hazardous Materials*, vol. 239–240, pp. 206–212, September 2012.
- [10] M. Ghaedi, A. Shokrollahi, K. Niknamb, E. Niknama, A. Najibi, and M. Soylakc, "Cloud point extraction and flame atomic absorption spectrometric determination of cadmium(II), lead(II), palladium(II) and silver(I) in environmental samples," *Journal of Hazardous Materials*, vol. 168, pp. 1022–1027, March 2009.
- [11] C. Ojeda, and F. Rojas, "Separation and preconcentration by a cloud point extraction producer for determination of metals: an overview," *Anal Bioanal Chem. Journal*, vol. 394, pp. 759-782, February 2009.
- [12] E. Pocurull, N. Fontanals, M. Calull, and C. Aguilar, "Chapter 20 - Environmental Applications, Handbooks in Separation Science," 591-641, 2020.
- [13] A. Appusamy, P. Purushothaman, K. Ponnusamy, and A. Ramalingam, "Separation of Methylene Blue Dye from Aqueous Solution Using Triton X-114 Surfactant," *Journal of Thermodynamics*, vol. 2014, pp. 1-16, 2014.
- [14] A. Gouda, and A. Amin, "Cloud-point extraction, preconcentration and spectrophotometric determination of trace quantities of copper in food, water and biological samples," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 120, pp. 88–96, 2014.
- [15] T. Gondim, J. Guedes, L. Ribeiro, G. Lopes, and W. Matos, "Optimization of a cloud point extraction procedure with response surface methodology for the quantification of dissolved iron in produced water from the petroleum industry using FAAS," *Marine Pollution Bulletin*, pp. 1-6, 2016.
- [16] N. Sato, M. Mori, and H. Itabashi, "Cloud point extraction of Cu(II) using a mixture of triton X-100 and dithizone with a salting-out effect and its application to visual determination," *Talanta*, vol. 117, pp. 376-381, December 2013.
- [17] A. Tabrizi, "Development of a cloud point extraction-spectrofluorimetric method for trace copper(II) determination in water samples and parenteral solutions," *Journal of Hazardous Materials*, vol. B139, pp. 260-264, January 2007.
- [18] L. Wang, J. Wang, Z. Zheng, and P. Xiao, "Cloud point extraction combined with high-performance liquid chromatography for speciation of chromium(III) and chromium(VI) in environmental sediment samples," *Journal of Hazardous Materials*, vol. 177, pp. 114-118, May 2010.
- [19] P. Racheva, N. Milcheva, F. Genc, and K. Gavazov, "A centrifuge-less cloud point extraction-spectrophotometric determination of copper(II) using 6-hexyl-4-(2-thiazolylazo) resorcinol," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 262, pp. 1-6, 2021.
- [20] M. Hashemi, S. Daryanavard, "Ultrasound-assisted cloud point extraction for speciation and indirect spectrophotometric determination of chromium(III) and (VI) in water samples," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 92, pp. 189-193, June 2012.
- [21] Y. El-Reash, H. Tantawy, E. Abdel-Latif, and W. Mortada, "Micelle-mediated extraction for speciation and spectrophotometric determination of iron using a newly synthesized salicylic acid derivative," *Microchemical Journal*, vol. 158, November 2020.
- [22] G. Matos, E. Reis, A. Costa, and S. Ferreira, "Speciation of chromium in river water samples contaminated with leather effluents by flame atomic absorption spectrometry after separation/preconcentration by cloud point extraction," *Microchemical Journal*, vol. 92, pp. 135-139, July 2009.
- [23] W. Mortada, I. Kenawy, M. Abdel-Rhman, G. El-Gamal, and S. Moalla, "A new thiourea derivative [2-(3-ethylthioureido)benzoic acid] for cloud point extraction of some trace metals in water, biological and food samples," *Journal of Trace Elements in Medicine and Biology*, vol. 44, pp. 266-273, December 2017.
- [24] A. Aswesi, R. Hussein, N. Bader, and R. Elkailany, "Propylene oxide-Ethylene oxide block polymer as a surfactant for separation of some metal ions from aqueous solution by cloud point extraction," *Adv. J. Chem. A*, vol. 3, pp. 259–264, 2020.
- [25] A. Asweisi, K. Algheryani, R. Hussein, "Separation of Cadmium from Aqueous Solutions by Cloud Point Extraction Using Different Non-ionic Surfactants," *The 3rd conf. on the environmental sciences, Misrata, Libya. 5-6 (Jun) 2022.* I. S. Jacobs and C. P. Bean, "Fine particles, thin films and exchange anisotropy," in *Magnetism*, vol. III, G. T. Rado and H. Suhl, Eds. New York: Academic, 1963, pp. 271–350.