

ECO-FRIENDLY EXTRACTION OF ACID BLACK 703 DYE FROM AQUEOUS SAMPLES USING DEEP EUTECTIC SOLVENT SYSTEM

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ABSTRACT

Aim of the study

A green and sustainable analytical method was developed for the extraction and determination of Acid Black 703 dye in aqueous samples using a natural deep eutectic solvent (DES)-based liquid–liquid microextraction coupled with UV-vis spectrophotometry. The DES, composed of choline chloride and phenol, was employed as an environmentally benign extraction medium, replacing conventional toxic organic solvents.

Material and methods

Critical experimental parameters, including pH, DES volume, sample-to-extractant ratio, and centrifugation time, were systematically optimized to maximize extraction efficiency.

Results and conclusions

Under optimal conditions (pH 6, 1 mL DES, 2 min centrifugation), the method exhibited good linearity in the range of 10–60 ppm, with a limit of detection (LOD) of 2.47 µg/L, and a limit of quantification (LOQ) of 7.50 µg/L. The relative standard deviation (RSD) ranged from 2.35% to 3.21%, confirming method precision. Application to real water samples demonstrated satisfactory recovery and reproducibility, highlighting the method's potential for routine monitoring of synthetic dyes in environmental matrices.

Keywords: Acid Black 703, deep eutectic solvent, dye removal, liquid-liquid micro extraction, wastewater treatment

INTRODUCTION

Dyes are widely used in the textile, cosmetic, leather, and food industries to color products, resulting in the generation of large volumes of wastewater containing synthetic pigments (Tkaczyk et al., 2020). Among the various synthetic dyes, Acid Black 703 is a sulfonated azo dye commonly used in textile and leather industries. Its water solubility and structural stability enable it to persist in wastewater, where

it can cause significant ecological and health risks (Gregory, 2000). Exposure to such dyes has been associated with allergic reactions, skin irritation, and possible mutagenic or carcinogenic effects. As a result, regulatory restrictions on the use and disposal of such dyes have increased, driving the demand for effective and sustainable dye removal technologies (Khan et al., 2023).

Several methods have been developed to address dye contamination in wastewater, including physi-

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cal, chemical, and biological approaches. Techniques such as adsorption, ion exchange, membrane filtration (e.g., nanofiltration and reverse osmosis), electrocoagulation, and advanced oxidation processes (e.g., ozonation and Fenton's reagent) have been extensively studied (Saravanan et al., 2022). While many of these methods are effective, they often suffer from limitations such as high operational costs, generation of secondary pollutants, complex procedures, or sensitivity to pH and ionic strength (Saravanan et al., 2021).

In recent years, the use of green solvents, particularly Deep Eutectic Solvents (DESs), has gained significant attention in the field of environmental remediation (Prabhune and Dey, 2023).

Although conventional solvents have been used extensively for dyes extraction, they have many drawbacks that seriously compromise safety, environmental impact, efficiency, and cost-effectiveness (Mariotti et al., 2020). Many of these solvents including acetone, methanol, and benzene show great toxicity, thereby endangering human health through possible respiratory issues, skin irritation, and even carcinogenic consequences with long-term use (Dirgha et al., 2019). Economically, the disposal of these hazardous solvents calls for expensive specialist treatment; their ineffective recovery and reuse compound operating costs (Blaney, 1986). Moreover, their generation from non-renewable petrochemical sources causes environmental contamination and resource depletion. Contributing to air pollution and ozone layer depletion as volatile organic compounds (VOCs), they also affect targeting certain colors effectively as the extraction procedure using common solvents sometimes suffers from poor selectivity and depends much on the underlying chemical characteristics of the dye. This stands somewhat apart from more flexible substitutes such as deep eutectic solvents (DES) (David and Niculescu, 2021).

Whereas deep eutectic solvent is broadly utilized in pharmaceutical, therapeutic, gas capturing and biodiversity for drug synthesis, drug delivery, air purification, biogas purification, bio catalysis, it has also been recently introduced in analytical chemistry for the extraction of dyes. To date, very few dyes have been extracted using different DES systems, therefore more exploration is required in that respect, in the

context of green extraction of dyes (Soltanmohammadi et al., 2021).

The main objective of the present study was to formulate a green DES-based extraction system composed of choline chloride (HBA) and phenol (HBD), combined with its evaluation as greener approach for the extraction of AB 703 dye by optimizing different parameters. The extraction efficiency of the DES was evaluated via UV-vis spectroscopy. The validation of this greener approach was performed in terms of limit of detection (LOD), limit of quantification (LOQ), and through calibration studies, and its practical applications have also been examined by analyzing spiked and real wastewater samples. This approach provides a cost-effective, environmentally friendly, and practical alternative for dye extraction, demonstrating the potential of DES-based LLME in industrial wastewater treatment applications.

MATERIALS AND METHODS

Material and reagents

Acid Black 703 dye, choline chloride (98% purity), tetrahydrofuran (99% purity), hydrochloric acid (HCl 37% purity), methanol, phenol, ammonium hydroxide, and NaOH were acquired from Merk Darmstadt (Germany). Tetrahydrofuran (THF) was used directly without dilution.

Instruments

Absorbance measurements were performed using a UV-vis spectrophotometer (UV-Vis 4000 spectrophotometer O.R.I Germany) with an absorption range of 200–800 nm. For shaking, the Vortex F202A0175 (Velp Scientifica, Pakistan) was utilized.

Other equipment included Centrifuge (Model 80-1 Electronic centrifuge) operated for extraction of dyes, a pH meter (Hanna HI2210) and digital balance (Aarson digital balance) for chemical weighing. For the purification of the water, a Millipore water deionizer (Merck Germany) was used.

DES preparation

The DES solution was prepared by mixing choline chloride and phenol in a ratio of 1:2. As choline chloride is hygroscopic, it was heated up to 85°C for 2 hours to eradicate humidity. Accurate amounts of

0.25 M phenol (23.52 g) and 0.13 M choline chloride (17.45 g) were weighed with the help of digital balance and poured into the beaker. Both components were mixed using magnetic stirrer at 64°C for 12 min, yielding a uniform mixture in the form of DES, which was subsequently utilized for Acid Black 703 extractions. To avoid contamination, the DES was covered with aluminum foil.

Validation assays and calculation formulas

To analyze the efficiency of deep eutectic solvent at optimized parameters; percent recovery (RE%) was calculated using the following equation:

$$RE\% = \frac{c_i - c_f}{c_i} \cdot 100 \quad (1)$$

where:

- RE – percent recovery,
- c_i – dye concentration before extraction,
- c_f – dye concentration after extraction.

The following equations were used to calculate LOD and LOQ:

$$LOD = \frac{3 \cdot SD}{m} \quad (2)$$

$$LOQ = \frac{10 \cdot SD}{m} \quad (3)$$

The equation shows the standard deviation of a linear curve, denoted by SD, and the slope, represented by m (Ul Haq et al., 2023).

The enrichment/pre-concentration factor was calculated using the EF factor equation:

$$EF = \frac{c_f}{c_i} \quad (4)$$

where:

- c_f – the final concentration of the analyte after extraction,
- c_i – the initial concentration of the analyte in the sample before extraction.

The relative standard deviation (RSD%) is used to express the accuracy of an assay. RSD% was calculated using the following formula:

$$RSD\% = \frac{SD}{c_m} \cdot 100 \quad (5)$$

where:

- SD – the standard deviation,
- c_m – the mean concentration value in real samples.

Procedure for preparing and extracting samples

To ensure the validity and practicality of the developed DES system, industrial and natural water samples were collected from Mardan River near Rashaki industrial estate, Mardan, Khyber Pakhtunkhwa, Pakistan, and tap water from University of Malakand, Chakdara, Khyber Pakhtunkhwa, Pakistan, respectively, in pre-washed glass bottles. In order to remove solid contamination, these samples were filtered and stored at room temperature. Since the water samples appeared to be colorless, the presence of targeted dye (AB703) was checked with the help of a spectrophotometer. Since no absorption was observed confirming the absence of AB 703, these samples were spiked with known concentration of AB 703 (10, 20, and 30 ppm) in 100 mL beaker separately. An amount 1 mL of the selected DES was added to the samples. Furthermore, 1 mL of THF was added as an emulsifying agent to improve the analyte recovery. The pH of the solution was adjusted by adding a buffer solution. Then the solution was mechanically shaken and centrifuged for 2 min at a speed of 4000 rpm for layer separation. The DES layer containing the analyte was extracted through a syringe and added to a new falcon tube. Then the remaining aqueous layer was examined through UV-visible spectrophotometer. The percent extraction from the samples was measured in order to illustrate the practical application of the proposed method at optimized conditions. To ensure the validity and efficiency of the proposed method, the analyses were carried out 3 times and percent extraction was calculated (Kołodnyńska et al., 2018).

RESULT AND DISCUSSION

Analysis of UV-vis absorption spectra and calibration curve

The spectral behavior of Acid Black 703 (AB 703) dye was examined in order to establish its characteristic absorption features, and construct a calibration curve

for quantitative analysis. The UV-vis absorption spectrum of a 20 ppm AB 703 solution exhibited a distinct and well-defined maximum absorption peak at 402 nm, indicating strong chromophoric activity in the visible region, and confirming the suitability of this wavelength for analytical measurements. The prominence and sharpness of the λ_{max} peak further demonstrate the dye's stable electronic transition, ensuring reliable absorbance readings during quantification.

To evaluate the linearity of the analytical response, a series of standard dye solutions (10–60 ppm) were measured at the established λ_{max} . The resulting calibration curve displayed an excellent linear relationship between absorbance and concentration, following the Beer–Lambert law across the entire tested range. The regression equation $y = 0.0054x + 0.0009$ with a correlation coefficient $R^2 = 0.9998$ reflects the high proportionality and minimal deviation in absorbance readings.

Analytical performance parameters were derived from the calibration data. The calculated limit of detection (LOD: 2.40 $\mu\text{g/L}$) and limit of quantification (LOQ: 7.50 $\mu\text{g/L}$) indicate strong method sensitivity, enabling the detection of AB 703 at trace levels. Additionally, the narrow confidence intervals and low variability among calibration points confirm the precision and reliability of the developed method.

Selection of DES solvent system for extraction of AB 703 dye

The most crucial step in an analytical method is choosing the proper solvent, which is determined by factors like cost-effectiveness, availability, high selectivity,

and recovery percentage during analyte extraction. For this reason, a new group of organic solvents called “deep eutectic solvents” (DESs) was chosen as fulfilling the above criteria (Makoś and Boczkaj, 2019). Four different DESs were tested to see which worked best for AB 703 extraction. Figure 2 shows the recovery percentages for each DES system used. A DES based on choline chloride (ChCl) and phenol (Ph) (1:2) produced the highest recovery (95%), whereas a DES-based on choline chloride and ethylene glycol (1:1) produced a 79% recovery. The ChCl + ethylene glycol-based DES recovered slightly less, although both DESs can extract AB 703. However, DESs based on choline chloride + phenol provided the highest recovery percentage because their strong hydrogen bonding makes them highly effective, improving solubility and extraction efficiency. Phenol has aromatic rings that interact with dye molecules through π - π interaction; furthermore, enhanced hydrophobic (phenol) and hydrophilic (choline chloride) characteristics allow them to extract a wide range of dyes.

Optimization of different extraction conditions for AB 703 dye

Effect of concentration

A series of dilute dye solutions were prepared, ranging from 10 to 60 ppm, while maintaining consistent parameters throughout the process. A specified amount of Deep Eutectic Solvent (DES) was precisely incorporated into each dye solution. Following equilibration, centrifugation was employed to recog-

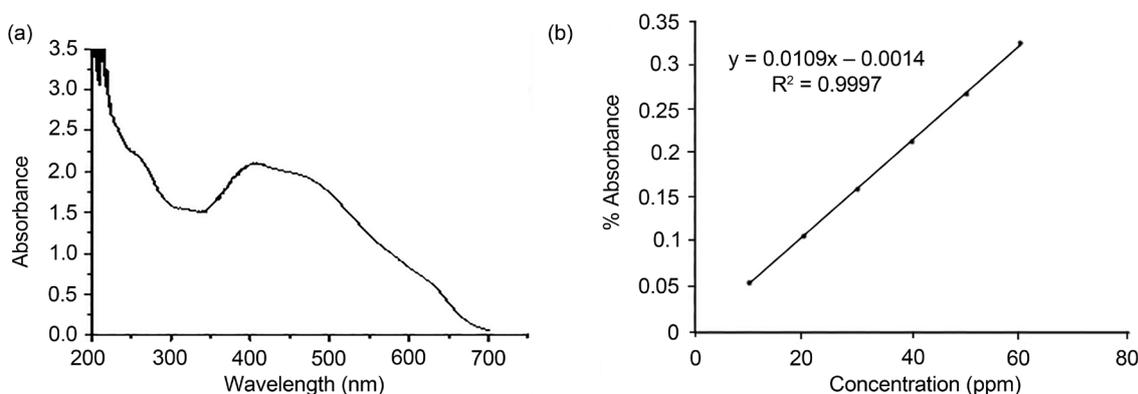


Fig. 1. a. Maximum absorption wavelength of AB 703 dye, b. Calibration curve for Acid Black 703

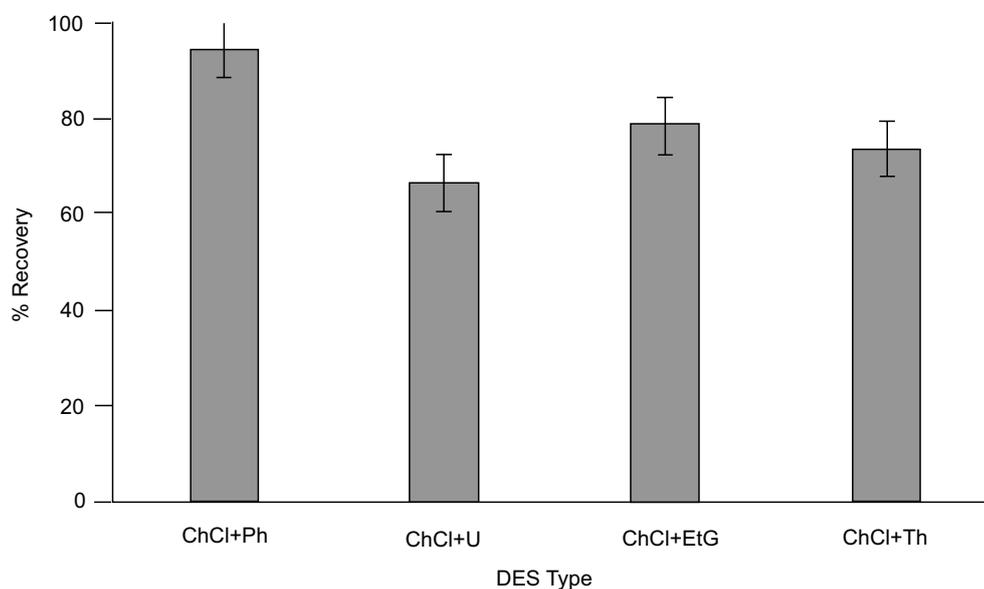


Fig. 2. Selection of the DES for maximum percent recovery. Analyte concentration 20 ppm; sample volume-20 mL; DES volume – 1 mL; THF volume 1mL; temperature 25°C, centrifugation time 2 min

nize the DES phase. The absorbance of the solutions was then recorded using a UV-vis spectrophotometer to determine the concentration of the aqueous phase. Figure 3a shows that the percentage extraction (%E) was considerably high at lower dye concentrations. However, as the dye concentration increased, there was a decline in the percentage of extraction (Qadaryah et al., 2019). The availability of active H bonding sites in the polar DES is associated with this phenomenon, facilitating more effective extraction at lower dye concentrations. In contrast, higher dye concentrations lead to increased aggregation of dye molecules, resulting in reduced extraction efficiency as the DES becomes saturated (Rahman, 2022). Although maximum extraction was recorded at 10 ppm, this concentration was considered too low, leading to the selection of 20 ppm as the ideal concentration for further research.

Effect of pH

When extracting from an aqueous media, it is essential to consider the pH value. Depending on the pH of the aqueous solution, the electrostatic interactions between chemical species may be strengthened or weakened. Therefore, the amount of analyte transported to the DES phase is directly influenced by pH (Ma and

Row, 2021; Sin, 2018). Furthermore, the extraction efficiency of DESs is impacted by pH. Therefore, in this study we proceeded to investigate how pH affected the movement of AB 703 from the aqueous phase to the DES phase. The pH of the medium was adjusted from 2 to 10 using phosphate buffer. To thoroughly examine the impact of pH on the extraction efficiency of DES, a pH meter was used to measure the sample's pH. Results for the pH optimization are displayed in Figure 3b. In a slightly acidic media (pH = 6), the highest percent extraction was obtained. Thus, the ideal pH of 6 was chosen. The pH directly influences the transfer of the analyte to the DES phase by altering the solubility and charge state of the analyte. At lower pH, the acidic dyes have a lower affinity to shift into an organic phase during extraction. At high pH levels, they are more likely to become protonated and water-soluble (Pei et al., 2007).

Effect of DES volume

DES is an essential component in the extraction process. Various quantities of DES were applied to the AB 703 dye samples to optimize the DES volume. Other factors, such as pH, DES ratio, and THF volume, were held constant for each sample. Six different Acid Black 703 dye samples at a concentration of 20 ppm were

utilized. 3 mL of each sample was collected and put in a separate falcon tube, adding 0.3, 0.5, 0.8, 1, 1.3, and 2 mL of DES volume. Following two minutes of centrifugation, the layers were separated and analyzed with a UV-visible spectrophotometer. It was demonstrated (Fig. 3c) that increasing the DES volume improved the extraction efficiency because of the high availability of solvent micro-droplets in DES (Li et al., 2020). Up to 1 mL, this rise in extraction percentage was restricted. The dye transfers between the DES and the aqueous phase was limited below the 1 mL volume of DES. Because of the diluting effect, increasing the DES volume further decreased the reaction.

Effect of THF

In the extraction process, THF increases the production of DES droplets carrying the target analyte. A substantial quantity of THF is required to complete DES emulsification. Six separate samples were collected for this purpose, and the optimal volume of THF as an emulsifying agent was determined to be 0.3, 0.5, 0.8, 1, 1.5, and 2 mL. The remaining parameters, such as pH, DES volume, and centrifugation duration, were kept constant across all samples. According to the results presented in Figure 3d, increasing the amount of THF to 1 mL enhanced the percentage extraction. Low volume of THF reduced the percentage extraction and resulted in an unsatisfactory emulsion. As the amount of THF increased, the percentage extraction decreased owing to dilution (Mohamadi et al., 2024). The highest amount of extraction of AB 703 was achieved with 1 mL of THF. As a result, 1 mL was deemed the most suitable volume to employ for future experiments.

Effect of centrifugation time

Centrifugation plays a crucial role in DES-based extraction by enhancing mass transfer, improving solvent extractability (Singh et al., 2020). The influence of centrifugation time was examined for the separation of DES and the aqueous phase. Centrifugation was used at 3500 rpm to separate the DES and aqueous phase (Liu et al., 2019). AB 703 dye was centrifuged for 1 to 5 minutes at various intervals to assess the extraction efficiency. After 2 minutes of centrifugation, the mixture had the highest percentage of AB 703 dye extracted. After that, the extraction percentage de-

creased when the centrifugation time was increased. Higher spinning times lead to reduced returns and dye degradation due to extended centrifuge exposure. The ideal centrifugation duration for more research was determined to be two minutes. The results are shown in Figure 3e.

Application of the method

The validity and applicability of this method were determined by analyzing the effect of dye concentration on the extraction of AB 703 from water that an industrial estate has contaminated. Water samples were collected from the Mardan River, Rashaki Industrial Estate, Khyber Pakhtunkhwa Pakistan, and the University of Malakand Khyber Pakhtunkhwa Pakistan. The samples were filtered and kept in plastic bottles for further experiments. The standard addition method was utilized in this experiment to determine the recovery for actual analyte samples. As no dye was found in the industrial aqueous sample, the sample were spiked with various known concentrations of the standard dye solution, i.e. from 10–30 ppm, allowing for accurate analysis. To calculate the relative standard deviation (%RSD), three analyses were performed for each spiked Industrial water sample. The results are given in Figure 4a, revealing a recovery of more than 93%. Similarly, the same procedure was applied to determine the percent recovery for the tap water sample. The tap water sample contained no dye, so it was spiked with different concentrations (10–30 ppm) from the stranded dye solution. Three analyses were carried out for each sample, and the results showed a recovery of more than 94% Figure 4b, indicating the deep eutectic solvent's accuracy and reliability.

Comparison with existing methods

The newly developed method was contrasted with the methodology outlined in the literature. As far as we know, few analytical methods are available for AB 703 analysis. Table 1 compares the technique and efficiency of the synthesized DES with earlier approaches reported in the literature.

From the table 1 we concluded that DES is a simple, economical, and eco-friendly process for dye extraction.

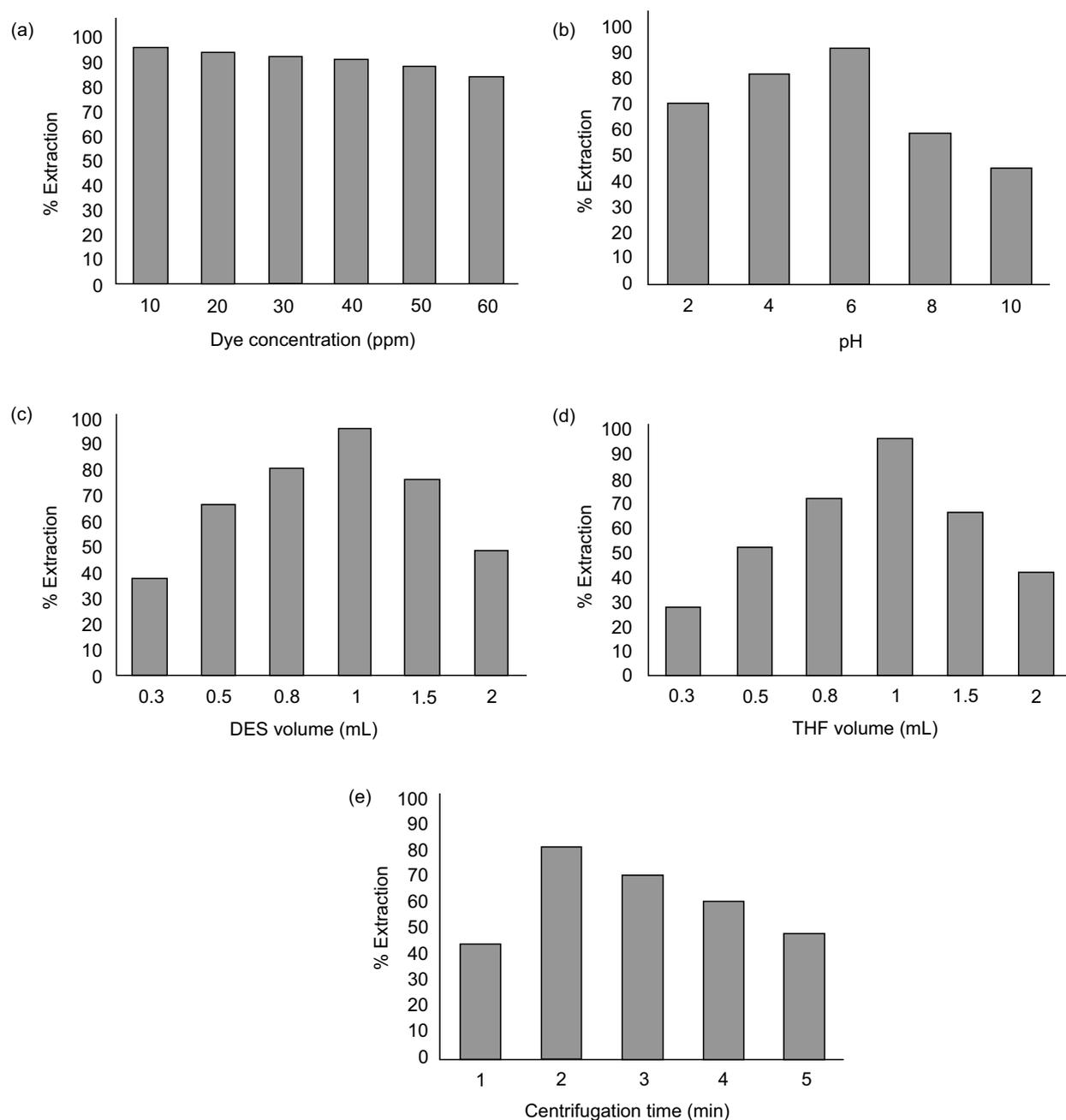


Fig. 3. a. The impact of dye concentration (ppm) on % extraction of AB 703 (pH = 6; THF volume = 1 mL; DES volume = 1 mL); b. The impact of pH on the % extraction of AB 703 (DES volume = 1 mL; THF volume 1 mL centrifugal time = 2 min; dye conc. = 20 ppm); c. Impact of DES volume (mL) on the % extraction of AB 703 (pH = 6; dye conc. = 20 ppm; THF volume = 1 mL; centrifugation time = 2 min); d. The impact of THF volume (mL) on the % extraction of AB 703 (pH = 6; dye conc. = 20 ppm; centrifugation time = 2 min; DES volume 1 mL); e. Impact of centrifugation time (min) on the % extraction of AB 703 (DES volume = 1 mL; pH = 6; dye conc. = 20 ppm; THF volume = 1 mL)

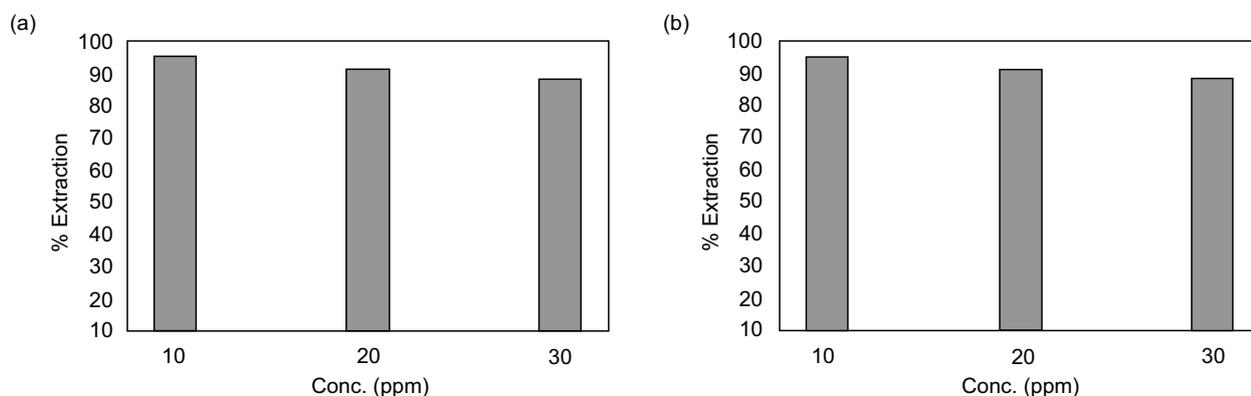


Fig. 4. a. Percent extraction of dyes from industrial water samples; b. Percent extraction of dyes from tap water samples

Table 1. Comparison of analytical methods and parameters for AB 703

Dye	Method	Agent	% Removal	Medium	Reference
Acid Black 703	Liquid-liquid Extraction	DES	91	Aqueous	Current work
	Bioremediation	<i>Pseudomonas aeruginosa</i>	71	Nutrient Broth Medium	(Khan et al., 2023)
	Molecularly Imprinted Polymers	MIPs Synthesized for Acid Black 703	87	Aqueous	(Ali et al., 2022)

CONCLUSION

This work describes a DES-based method for extracting Acid Black 703 dye from an aqueous medium, where a spectrophotometer was used to detect and quantify the dye. The analyzed Deep Eutectic Solvent (DES) of phenol and choline chloride (2:1) was the best green solvent for dye extraction. Acid Black 703 dye was efficiently extracted from an aqueous medium using DES solvent for spectrophotometric analysis. The method demonstrated a recovery efficiency of 93–96.9%, with a linearity range of (10–60 ppm). The technique is precise, with (LOD) of 2.40 µg/L. The solvent was used for real water sample analysis. The developed method is advantageous due to its shortened extraction time and robustness. This method is notable for using green solvents, which are more efficient and have a lower environmental impact. This is the first reported method using Deep Eutectic Solvents (DES) specifically for the extraction of Acid Black 703 dye.

REFERENCES

- Ali, F., Shah, Z., Khan, A., Saadia, M., Al Othman, Z.A., Cheong, W.J. (2022). Synthesis, column packing and liquid chromatography of molecularly imprinted polymers for the acid black 1, acid black 210, and acid brown 703 dyes. *RSC Advances*. 12(30), 19611–19623. <https://doi.org/10.1039/d2ra02357a>.
- Blaney, B.L. (1986). Treatment Technologies for Hazardous Wastes: Part II Alternative Techniques for Managing Solvent Wastes. *Journal of the Air Pollution Control Association*, 36(3), 275–285. <https://doi.org/10.1080/00022470.1986.10466070>.
- David, E., Niculescu, V.-C. (2021). Volatile organic compounds (VOCs) as environmental pollutants: occurrence and mitigation using nanomaterials. *International Journal of Environmental Research and Public Health*, 18(24), 13147.
- Dirgha, R., Nisha, A. (2019). An Overview on Common Organic Solvents and Their Toxicity. *Journal of Pharmaceutical Research International*, 1–18. <https://doi.org/10.9734/jpri/2019/v28i330203>.

- Gregory, P. (2000). Dyes and dye intermediates. *Kirk-Othmer Encyclopedia of Chemical Technology*, 1–66. <https://doi.org/10.1002/0471238961.0425051907180507.a01.pub2>.
- Hou, Y.C., Yao, C.F., Wu, W.Z. (2018). Deep eutectic solvents: green solvents for separation applications. *Acta Phys.-Chim. Sin*, 34(8), 873–885.
- Khan, M.D., Singh, A., Khan, M.Z., Tabraiz, S., Sheikh, J. (2023). Current perspectives, recent advancements, and efficiencies of various dye-containing wastewater treatment technologies. *Journal of Water Process Engineering*, 53, 103579. <https://doi.org/10.1016/j.jwpe.2023.103579>.
- Kołodziejka, D., Hubicki, Z., Majdan, M., Wawrzkiwicz, M., Gładysz-Płaska, A., Wołowicz, A. (2018). Optimization of methods for removing various types of pollutions from model solutions and wastewaters. *Europe*, 26, 108.
- Li, Y., Li, X., Tang, S., Yang, Y. (2020). Emulsification liquid-liquid micro-extraction based on natural deep eutectic solvent for (triarylmethane) dyes determination. *Chemical Papers*, 74(10), 3617–3626. <https://doi.org/10.1007/s11696-020-01184-4>.
- Liu, X., Liu, C., Qian, H., Qu, Y., Zhang, S., Lu, R., Gao, H., Zhou, W. (2019). Ultrasound-assisted dispersive liquid-liquid microextraction based on a hydrophobic deep eutectic solvent for the preconcentration of pyrethroid insecticides prior to determination by high-performance liquid chromatography. *Microchemical Journal*, 146, 614–621. <https://doi.org/10.1016/j.microc.2019.01.048>.
- Ma, W., Row, K.H. (2021). pH-induced deep eutectic solvents based homogeneous liquid-liquid microextraction for the extraction of two antibiotics from environmental water. *Microchemical Journal*, 160, 105642.
- Makoś, P., Boczkaj, G. (2019). Deep eutectic solvents based highly efficient extractive desulfurization of fuels—Eco-friendly approach. *Journal of Molecular Liquids*, 296, 111916. <https://doi.org/10.1016/j.molliq.2019.111916>.
- Mariotti, N., Bonomo, M., Fagiolari, L., Barbero, N., Gerbaldi, C., Bella, F., Barolo, C. (2020). Recent advances in eco-friendly and cost-effective materials towards sustainable dye-sensitized solar cells. *Green Chemistry*, 22(21), 7168–7218.
- Mohamadi, S., Esfandiari, Z., Khodadadi, M., Dehaghani, M.S.T. (2024). Simultaneous analysis of benzoic and sorbic acids in orange juice using thymol/water natural deep eutectic solvent and DLLME method followed by high performance liquid chromatography. *Journal of Food Measurement and Characterization*, 18(7), 6285–6294. <https://doi.org/10.1007/s11694-024-02647-y>
- Pei, Y.C., Wang J.J., Xuan, X.P., Fan, J., Fan, M. (2007). Factors Affecting Ionic Liquids Based Removal of Anionic Dyes from Water. *Environmental Science & Technology*, 41(14), 5090–5095. <https://doi.org/10.1021/es062838d>.
- Prabhune, A., Dey, R. (2023). Green and sustainable solvents of the future: Deep eutectic solvents. *Journal of Molecular Liquids*, 379, 121676. <https://doi.org/10.1016/j.molliq.2023.121676>.
- Qadaryah, L., Azizah, N., Syafa'atullah, A.Q., Bhuana, D.S., Mahfud, M. (2019). The Extraction of Natural Dyes from Henna Leaves (*Lawsonia inermis* L.) by Ultrasound-assisted Method. *IOP Conference Series: Materials Science and Engineering*, 543(1), 012082. <https://doi.org/10.1088/1757-899X/543/1/012082>.
- Rahman, M.S. (2022). Formulation, Structure, and Applications of Therapeutic, Amino Acid, and Water-Based Deep Eutectic Solvents. South Dakota State University.
- Saravanan, A., Deivayanai, V.C., Kumar, P.S., Rangasamy, G., Hemavathy, R.V., Harshana, T., Gayathri, N., Alagumalai, K. (2022). A detailed review on advanced oxidation process in treatment of wastewater: Mechanism, challenges and future outlook. *Chemosphere*, 308, 136524. <https://doi.org/10.1016/j.chemosphere.2022.136524>.
- Saravanan, A., Senthil Kumar, P., Jeevanantham, S., Karishma, S., Tajsabreen, B., Yaashikaa, P.R., Reshma, B. (2021). Effective water/wastewater treatment methodologies for toxic pollutants removal: Processes and applications towards sustainable development. *Chemosphere*, 280, 130595. <https://doi.org/10.1016/j.chemosphere.2021.130595>.
- Singh, A., Kaur, R., Kumar, P., Tanwar, A. (2020). Yam. In: G.A. Nayik, A. Gull (eds.) *Antioxidants in Vegetables and Nuts – Properties and Health Benefits*. Singapore, Springer Singapore, 291–307.
- Soltanmohammadi, F., Jouyban, A., Shayanfar, A. (2021). New aspects of deep eutectic solvents: extraction, pharmaceutical applications, as catalyst and gas capture. *Chemical Papers*, 75(2), 439–453. <https://doi.org/10.1007/s11696-020-01316-w>.
- Tkaczyk, A., Mitrowska, K., Posyniak, A. (2020). Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review. *Science of the Total Environment*, 717, 137222. <https://doi.org/10.1016/j.scitotenv.2020.137222>.
- Ul Haq, H., Wali, A., Safi, F., Arain, M.B., Kong, L., Boczkaj, G. (2023). Natural deep eutectic solvent based ultrasound assisted liquid-liquid micro-extraction method for methyl violet dye determination in contaminated river water. *Water Resources and Industry*, 29, 100210. <https://doi.org/10.1016/j.wri.2023.100210>.

EKOLOGICZNA EKSTRAKCYJA BARWNIKA ACID BLACK 703 (CZERŃ KWASOWA) Z PRÓBEK WODNYCH Z WYKORZYSTANIEM UKŁADU GŁĘBOKO EUTEKTYCZNYCH ROZPUSSZCZALNIKÓW

ABSTRAKT

Cel badań

W ramach badań opracowano przyjazną środowisku, zrównoważoną metodę analityczną, służącą do ekstrakcji i oznaczania barwnika Acid Black 703 (czerń kwasowa) w próbkach wodnych. Opracowana metoda wykorzystuje mikroekstrakcję ciecz–ciecz na bazie naturalnego głęboko eutektycznego rozpuszczalnika (DES), w połączeniu ze spektrofotometrią UV-vis. Rozpuszczalnik DES, składający się z chlorku choliny i fenolu, zastosowano jako przyjazne dla środowiska medium ekstrakcyjne, zastępujące konwencjonalne, toksyczne rozpuszczalniki organiczne.

Materiał i metody

Krytyczne parametry doświadczalne (takie jak: współczynnik pH, objętość DES, stosunek masy próbki do objętości rozpuszczalnika oraz czas wirowania) zostały poddane systematycznej optymalizacji, tak by ekstrakcja była możliwie jak najbardziej skuteczna.

Wyniki i wnioski

W optymalnych warunkach (współczynnik pH 6, objętość DES 1 ml, wirowanie przez 2 minuty) metoda charakteryzowała się dobrą liniowością w zakresie 10–60 ppm, z granicą wykrywalności (LOD) wynoszącą 2,47 µg/l oraz granicą oznaczalności (LOQ) wynoszącą 7,50 µg/l. Względne odchylenie standardowe (RSD) wahało się w przedziale od 2,35% do 3,21%, co świadczy o dużej dokładności badanej metody. Zastosowanie metody do rzeczywistych próbek wody wykazało odzysk na zadowalającym poziomie. Co więcej, podczas testowania uzyskano powtarzalność pomiarową. Pozwala to stwierdzić, że zaproponowana metoda ma duży potencjał w kontekście rutynowego monitorowania barwników syntetycznych w środowisku.

Słowa kluczowe: Acid Black 703 (czerń kwasowa), rozpuszczalnik głęboko eutektyczny (DES), usuwanie barwników, mikroekstrakcja ciecz–ciecz, oczyszczanie ścieków