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Environmental Remediation of Dye-Contaminated Water Using Epoxy Resin-Based Molecularly Imprinted Polymers for Selective Solid-Phase Extraction of Methylene Blue from Binary Dye Systems

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Abstract

In recent years, increasing discharge of dye-containing industrial wastewater has become a major environmental concern because of its adverse effects on aquatic ecosystems and water quality. In this study, epoxy resin-based molecularly imprinted polymers (ER-MIPs) were successfully synthesized and characterized as selective sorbents for the environmental remediation and removal of methylene blue (MB) from aqueous dye systems using molecularly imprinted solid-phase extraction (MISPE). Methylene blue was employed as the template molecule to fabricate selective recognition sites capable of enhancing extraction selectivity and efficiency in binary dye systems. Several operational parameters affecting extraction performance, including eluent type and volume, flow rate, sorbent amount, dye concentration, sample volume, and pH, were systematically optimized to maximize dye removal efficiency. The optimum conditions were achieved using methanol/acetic acid/water (8:1:1, v/v/v) as eluent, 15 mL eluent volume, 0.1 g sorbent mass, 100 mg L^{-1} MB concentration, and neutral pH conditions (pH 7). Under these conditions, ER-MIP exhibited significantly higher extraction performance than the corresponding non-imprinted polymer (ER-NIP), owing to the formation of selective recognition cavities, with removal efficiencies ranging from 89.13% to 94.76% and imprinting factors between 4.55 and 8.83. The findings demonstrate the potential applicability of ER-MIPs as selective, efficient, and environmentally relevant sorbents for dye-contaminated water treatment and wastewater remediation.

Keywords: Molecularly imprinted polymers (MIPs), Methylene blue, Solid-phase extraction, Epoxy resin, Environmental remediation.

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1. Introduction:

Organic pollutants continuously pose a growing environmental challenge. Effluents from the chemical, dyeing, pharmaceutical, and paper industries have been identified as having persistent organic pollutants. Hence, there is a need to devise viable and cost-efficient strategies to mitigate these challenges (Li et al., 2023; Mustafa et al., 2024). Some synthetic dyes contain dangerous elements, such as heavy metals and chemicals associated with cancer, which can be extremely harmful, especially with long-term exposure or consumption(Mongkholrattanasit et al., 2011) Once wastewater dyes are released into water bodies, they become effluents of various vibrant colors that are highly damaging to ecosystems. Dyes greatly reduce water quality by blocking sunlight, disrupting photosynthesis, or even killing aquatic life. Most dyes are aromatic, which increases the toxicity of the effluent and makes it more resistant to degradation(Khodayari et al., 2024).

There have been cases where methylene blue (MB) poisoning has been known to have negative impacts on human health, leading to symptoms such as an elevated heartbeat, nausea, and vomiting. MB dye, leading to reduced photosynthesis activity and increased chemical oxygen demand COD (Aniagor et al., 2021; Rápó & Tonk, 2021). Various Physical, biological, and chemical methods are used to remove dyes from effluents (Ali et al., 2023; Aragaw & Bogale, 2023; Bilińska et al., 2016; Dobrosz-Gómez et al., 2024; Gad et al., 2023; Greluk & Hubicki, 2013; Lin et al., 2016; Thamer et al., 2020; Zang et al., 2024). Even though the proposed methods have been found effective in removing dyes, they are not very specific because they rely solely on non-selective adsorption mechanisms, which ultimately lead to poor specificity for dyes. Therefore, it is very important to develop highly effective methods for removing dyes from wastewater. In this respect, molecular imprinting polymers (MIPs) have been proposed for the effective removal of toxic substances, such as dyes, from wastewater. MIPs are considered cost-effective adsorbents/sorbents with strong prospects for future applications. Additionally, MIPs are considered safer for the environment than other methods. MIPs are also very effective in harsh environmental conditions. They are also chemically, mechanically, and thermally very stable. MIPs are also very easy to reproduce, with long lifecycles that allow repeated use without loss of efficiency (Liu et al., 2016; Salur-Can et al., 2017).

Unlike traditional carbon-based sorbents, MIPs can be designed to have high selectivity for capture, even at lower concentrations(de León-Martínez et al., 2018).

To optimize the efficacy and selectivity of solid-phase extraction (SPE), molecularly imprinted polymers (MIPs) can be used. Such an amalgamation of both methods is referred to as molecularly imprinted solid-phase extraction (MISPE)(Garcinuño et al., 2023; Xolo & Mahlambi, 2024).

The SPE techniques, in particular, have attracted substantial interest for their versatility and flexibility in a wide range of sample matrices, exceptional ability to remove matrix interferences, thereby improving analytical sensitivity, selectivity, and overall performance (Płotka-Wasylka et al., 2023; Rosendo et al., 2023).

The objective of this research is to synthesize and test molecularly imprinted polymers (MIPs) for selectively extracting and removing methylene blue (MB) from aqueous solutions using molecularly imprinted solid-phase extraction (MISPE). This is accomplished by optimizing various parameters in the preparation of MIPs, such as pH, sorbent quantity, and flow rate, to obtain maximum adsorption capacity. Furthermore, the selectivity of these synthesized MIPs towards methylene blue dye in the presence of other dyes is also evaluated. The proposed method should provide a selective, economical, and eco-friendly procedure for eliminating dye contaminants from water.

2. Experimental

2.1 Materials:

Epoxy resin and ethylenediamine were obtained from BHD (UK). Polyethylene glycol 400 (PEG-400) and Sodium hydroxide were supplied by Merck (Germany). Methanol and toluene were purchased from SDFCL (India); acetic acid was purchased from Honeywell/Fluka; and hydrochloric acid was obtained from GCC. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were obtained from SRI. Ethanol was supplied by RCI. Methylene Blue trihydrate and the competing dyes (Trypan Blue, Crystal Violet, Congo Red, Brilliant Green, Eriochrome Black T) were obtained from HiMedia (India). All chemical substances used in the study were of analytical purity grade and used as received. All aqueous solutions were prepared using distilled water.

The instruments used in the present study included a Digital Sensitive Balance (BL2015-Sartorius, Germany), Drying Oven (ISO, CE, GMP, FDA type, Japan) Infrared Spectrophotometry (ALPHA II, Germany), pH meter (SD 300 PH, Germany), Solid-phase extraction (SPE) cartridge (India). Thermogravimetric Analysis instrument (TGA-Q50, USA), Ultrasonic Cleaner (Tefic Biotech, China), UV-Visible Spectrophotometer (T80 EMC-LAB, UK).

2.2 Preparation of molecular imprinting polymers

An Epoxy-based Molecularly Imprinted Polymer (MIP) was prepared, with methylene blue as the template molecule. To do this, 5 g of Epoxy resin was combined with 2.5 g of ethylenediamine (the curing agent), 2 g of polyethylene glycol (the porogenic agent), and 0.03 g of methylene blue. The mixture was kept at room temperature for 24 h, then heated at 85 °C for 3 h to complete the polymerization. The polymer produced was then crushed to get particles of uniform size, followed by selective template extraction to create binding sites.

For the non-imprinted polymer (NIP), the procedure was the same, except that methylene blue was not added.

2.3 Template Extraction:

After the synthesis of the molecularly imprinted polymers (MIPs), the removal of the methylene blue template molecules from the molecularly imprinted polymers was carried out by washing the molecularly imprinted polymer with a mixture of methanol, acetic acid, and water (8:1:1, v/v/v)(Asman et al., 2012). This washing process was carried out sequentially several times with 50 mL of the washing mixture and ultrasound agitation. The removal of the methylene blue template molecules was monitored daily by measuring the amount of remaining dye until complete removal.

2.4 Solid Phase Extraction Procedure

The SPE technique follows a specific sequence of steps. These include conditioning the column, loading the sample onto the column, and eluting the sample(Cherkashina et al., 2020; Xolo & Mahlambi, 2024). A polypropylene tube is used as the SPE cartridge. A filter paper is then packed into the column. Subsequently, 0.5 g of EP-MIP and the corresponding non-imprinted polymers, EP-NIP, are packed into the SPE column. A filter paper is used to cover the sorbent.

The SPE column is conditioned by passing 5 mL of deionized water through it. The dye solution is then passed through the SPE column under gravity flow. The dye molecules will be adsorbed onto the sorbent. Subsequently, the eluate is collected from the SPE column. The eluate is analysed to determine the dye concentration.

The recovery percentage (%) was calculated as per Eq. 1.

$$(\%)\ Recovery = \frac{(C_{initial} - C_{remaining})}{C_{initial}} \times 100 \quad \ldots Eq. 1$$

Where: $C_{initial}$: Initial concentration of the dye before adsorption, and $C_{remaining}$: Remaining concentration of the dye after adsorption.

2.5 Optimization of SPE Conditions

The SPE conditions were optimized by varying one condition at a time while keeping the others constant to maximize recovery(Saleh, Abdulwahid, & Kadhim, 2024; Saleh, Abdulwahid, & N. Kadhim, 2024)

2.5.1 Effect of Eluent Type and Volume

The effect of eluent type on desorption recovery was studied using solvents such as dimethyl sulfoxide (DMSO), methanol, ethanol, and dimethylformamide (DMF), as well as a methanol-acetic acid-distilled water mixture (8:1:1 v/v/v). Eluent volumes ranging from 5 to 25 mL were tested to determine the optimal conditions for maximum dye recovery.

2.5.2 Effect of Flow Rate

To optimize the SPE process, experiments were conducted at flow rates ranging from 1.25 to 5 mL/min. In all experiments, the other parameters, such as the polymer mass, dye solution volume, dye concentration, and pH, were kept constant.

2.5.3 Effect of Sorbent Amount

In this experiment, the effect of sorbent amount on extraction efficiency was investigated using ER-MIP and ER-NIP at amounts ranging from 0.1g to 2.5 g. During this experiment, other factors such as dye concentration, sample solution, and pH were kept constant as per the general procedure.

2.5.4 Effect of Dye Concentration

In this experiment, the effect of methylene blue concentration on extraction efficiency using ER-MIP and ER-NIP polymers, ranging from 100 to 500 mg L^{-1}, was investigated. During this experiment, the sample solution and pH were kept constant.

2.5.5 Effect of Sample Volume

The effect of dye solution volume on SPE efficiency was studied by varying the sample volume from 5 to 50 mL. In all cases, the column was packed with 0.1 g of ER-MIP and EP-NIP.

2.5.6 Effect of pH

To investigate the effect of solution pH on SPE performance, experiments were conducted over a pH range of 2 to 12. In these experiments, the column was packed with the optimized mass of sorbent material, and the dye solution at the previously determined optimal concentration and volume was passed through the column at different pH values. Subsequently, the previously determined optimal eluent was used to elute the retained dye.

2.6 Preparation of Calibration Curve for MB and Competing Dyes:

Calibration curves of Methylene Blue (MB) and competing dyes, including Brilliant Green (BG), Trypan Blue (TB), Crystal Violet (CV), Congo Red (CR), and Eriochrome Black T (EBT), were obtained in the linear concentration range by applying the Beer-Lambert law using a UV-Visible spectrophotometer. The measurements were done at the λmax value of each dye. The experimentally calculated values of λmax were 664 nm for MB, 625 nm for BG, 600 nm for TB, 580 nm for CV, 500 nm for CR, and 530 nm for EBT. Besides, the competing dyes were also studied at MB's λmax, and MB was studied at the λmax of the competing dyes. This was done to determine the binary systems of dye concentrations using the Beer-Lambert equation and to assess the selectivity behavior of the synthesized polymers.

2.7 Selectivity Evaluation:

The selectivity of the ER-MIP and ER-NIP was evaluated by studying the capability of the synthesized MIP to remove the template dye methylene blue (MB) in the presence of several other competing dyes with diverse structures, including brilliant green (BG), trypan blue (TB), Congo red (CR), crystal violet (CV), and Eriochrome Black T (EBT). The efficiency of the ER-MIP was later compared with the efficiency of the ER-NIP. The absorbance of the dye mixture was measured using λmax for both MB and its corresponding competitor. The removal efficiency, distribution coefficient, selectivity coefficient, and imprinting factor were computed.

3. Results and Discussion

3.1 Fourier-transform infrared spectroscopy (FT-IR):

Fig. 1 and Fig. 2 show the FTIR spectra of ER-NIP and ER-MIP, respectively. The absence or reduction of the epoxy characteristic band at 915 cm^{-1} indicated ring-opening polymerization reactions in the curing process. The vibrations at 1235 cm^{-1} and 1240 cm^{-1} were attributed to asymmetric aromatic C-O stretch vibration for ER-NIP and ER-MIP, respectively. In addition, the vibration at 1501 cm^{-1} and 1506 cm^{-1} was due to aromatic C-C stretch vibration of ER-NIP and ER-MIP, respectively. The asymmetric stretching vibrations of the CH_3 group were recorded at 2922–2925 cm^{-1}. On the other hand, the OH stretch vibration moved from 3422 cm^{-1} to 3401 cm^{-1} in ER-NIP and ER-MIP, respectively(González et al., 2012; Nikolic et al., 2010).

Table 1: The important main bands ER-NIP and ER-MIP

Functional groups	Frequency (cm^{-1})	
	ER-NIP	**ER-MIP**
C-O stretch	1235	1240
C-C stretching vibration in aromatic rings	1501	1506
asymmetrical C-H stretch of the $–CH_3$ group	2925	2922
OH	3422	3401

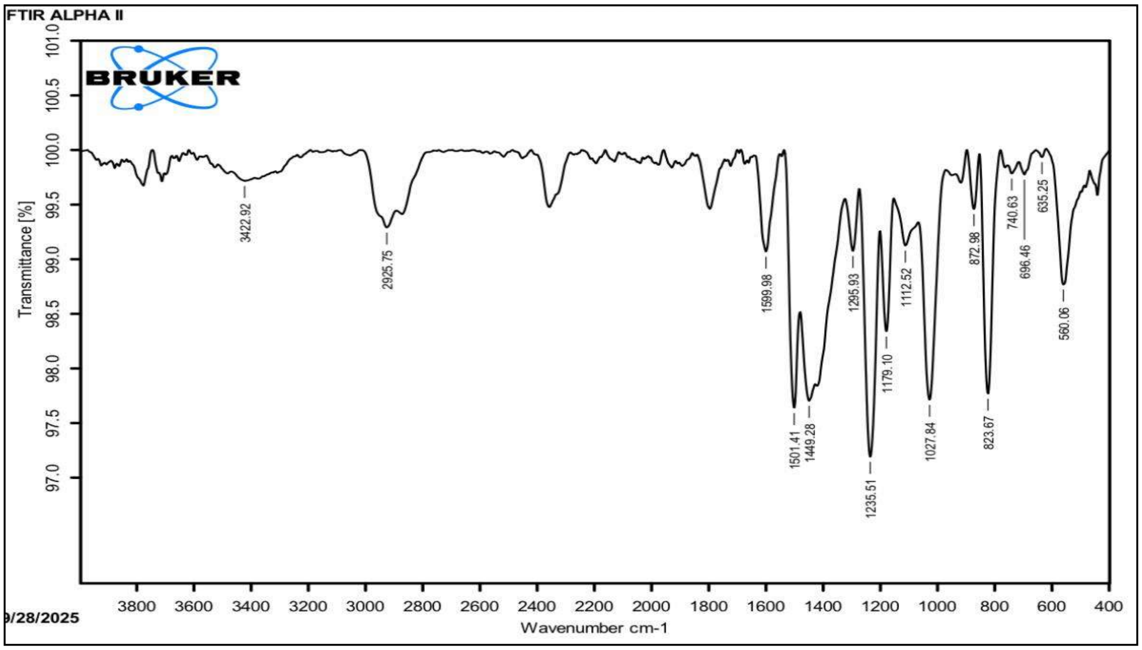

Fig. 1: FT-IR spectrum of ER-NIP.

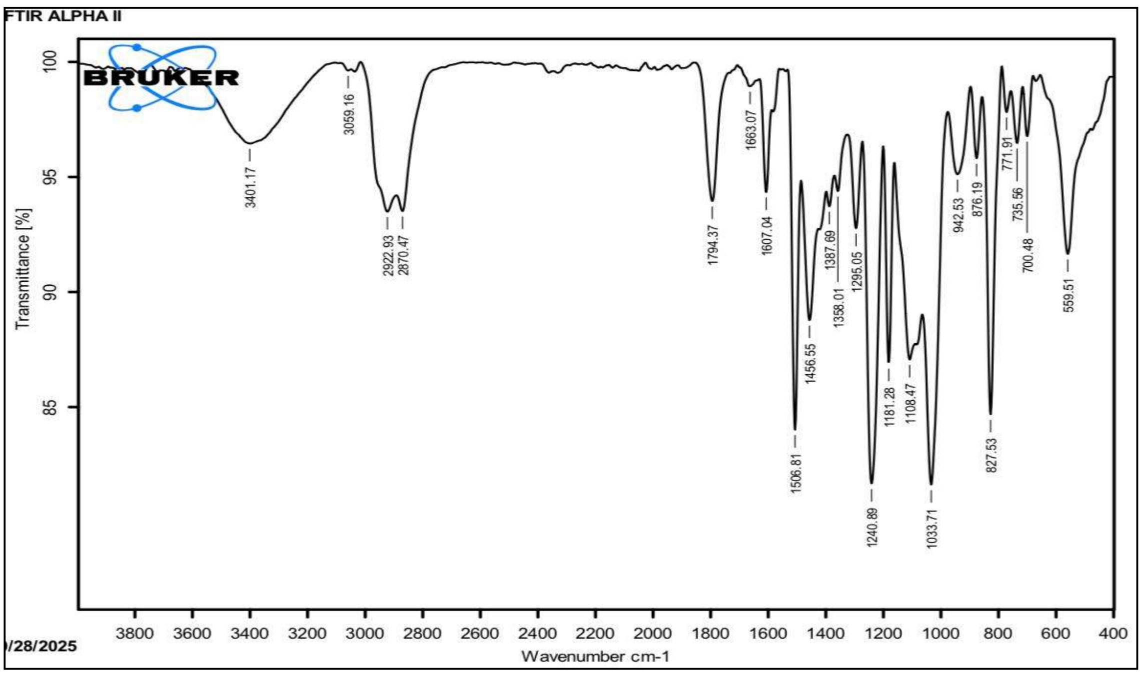

Fig.2: FT-IR spectrum of ER-MIP.

3.2 Thermal stability study of NIPs and MIPs:
Thermogravimetric analysis and differential thermogravimetric (DTG) analysis were used to determine the thermal stability of the synthesized polymers by measuring weight loss as a function of temperature at a fixed heating rate(Gikarakis et al., 2021)

TGA and DTG graphs of ER-NIP are illustrated in Fig. 3. In this regard, the thermal degradation of the epoxy resin is observed in two steps. The first degradation step occurs at Tmax = 186 °C and is accompanied by a slight weight loss, attributed to the decomposition of the aliphatic chain of the polyamine hardener. In the second step, the process occurs at Tmax = 409 °C, accompanied by significant weight loss due to decomposition of the epoxy resin network. The last stage of degradation could include reactions such as isomerization, intramolecular ring closure, chain transfer, and other radical-based decomposition reactions.(Mansour et al., 2022)

The TGA and DTG results of ER-MIP are provided in Fig. 4. A thermal decomposition pattern similar to that of ER-NIP was observed, and the decrease in the first-step decomposition temperature was attributed to the interaction between the amine group of the hardener and the functional groups of the template molecules.

Table 2: Decomposition temperatures of prepared MIP and NIP

NIP and MIP	Decomposition temperature °C	
	1st stage T °C	2nd stage T°C
ER-NIP	186	409
ER-MIP	167	407

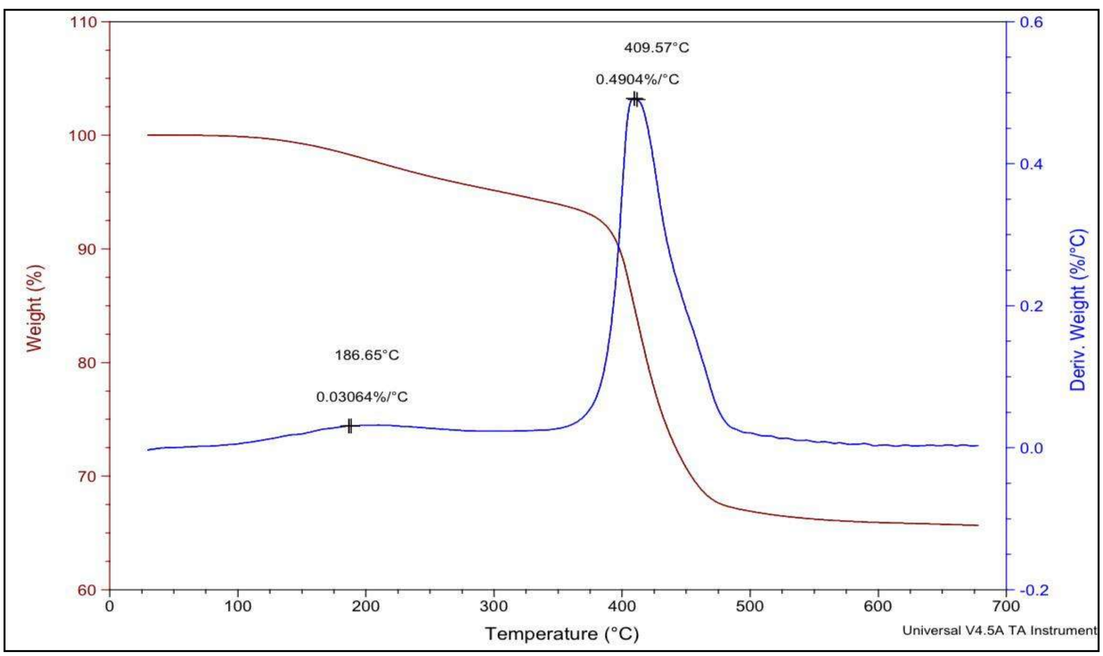

Fig. 3: TGA Thermogram of ER-NIP

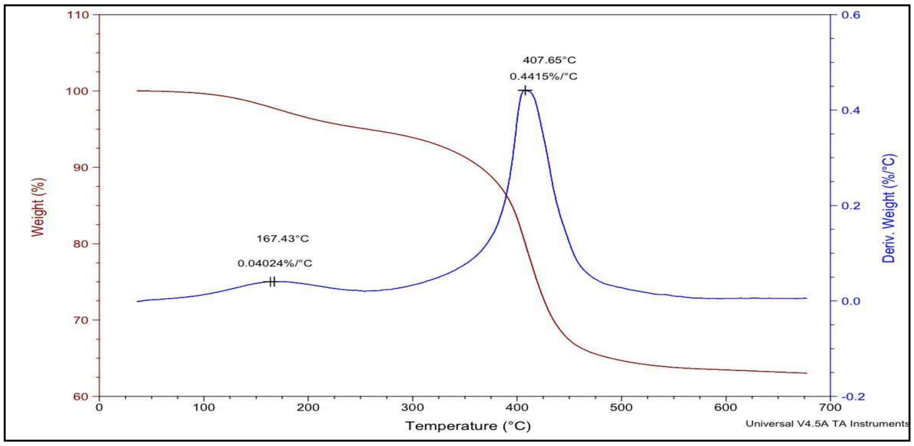

Fig.4: TGA Thermogram of ER-MIP

3.3 Optimization of SPE:

SPE Optimization was performed using the single-factor approach, in which each parameter was varied individually while keeping all others constant(Munzhelele et al., 2025). The removal percentage (%R) was used to evaluate the efficiency of adsorption of the polymers, which was mathematically represented as follows:

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{.... Eq. 2}$$

In this expression, C_O and C_e denote the initial and residual concentrations at equilibrium

3.3.1 Effect of Eluent Type:

In this study, the influence of different eluent solvents on the extraction of methylene blue from ER-MIP and ER-NIP was explored using DMF, DMSO, methanol, ethanol, and a ternary solvent mixture of methanol, acetic acid, and water (8:1:1). It has been revealed that the ternary solvent mixture showed better extraction efficiency than another solvent systems Fig.5. The improved extraction could be due to the synergistic effects of solvent components, in which methanol promotes dye solubility and acetic acid inhibits hydrogen bonding between dyes and the matrix (Omidi et al., 2014). In turn, DMSO, DMF, methanol, and ethanol are less efficient than the ternary solvent system because they are ineffective at disrupting interactions between dye molecules and the polymer matrix.

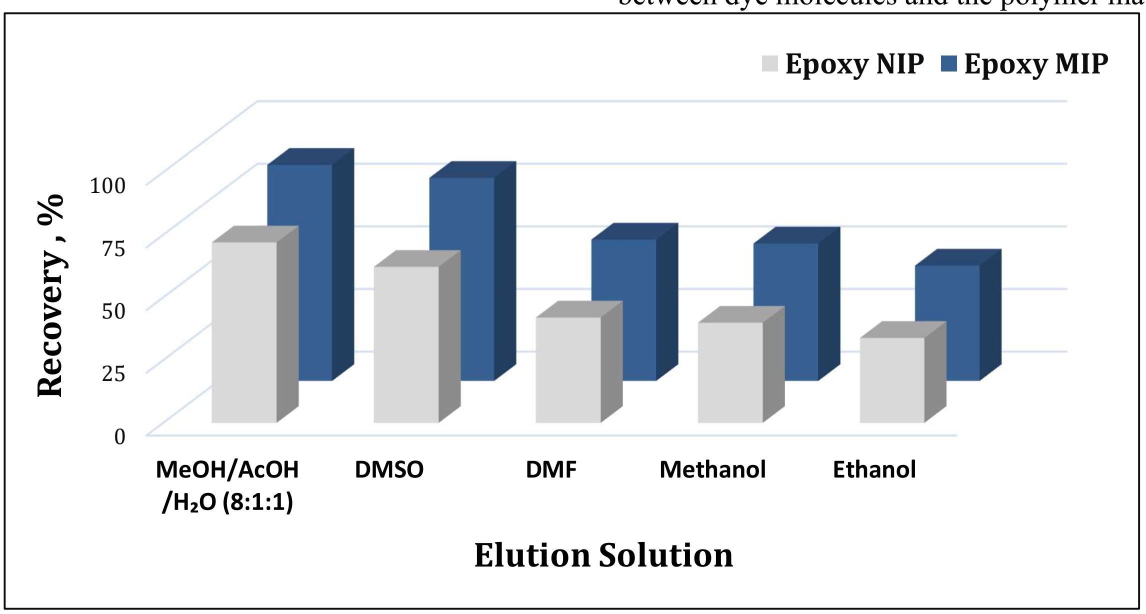

Fig.5: Effect of eluent type on the extraction recovery (%) of epoxy resin.

3.3.2 Effect of Eluent Volume:

The effect of solvent volume on recovery percentage (%R) was evaluated from 5 mL to 25 mL, with all other variables held constant, including pH, dye concentration, dye volume, sorbent weight, and flow rate, following the general extraction process. As illustrated in Fig. 6, the % Recovery increases with increasing solvent volume until it reaches a saturation point. If the solvent volume used is relatively low, partial desorption of methylene blue occurs, thereby preventing it from breaking the bonds formed between the dye molecules and polymer binding sites. The maximum % Recovery was achieved at a solvent volume of 15 mL for both ER-MIP and ER-NIP (Cheng et al., 2024).

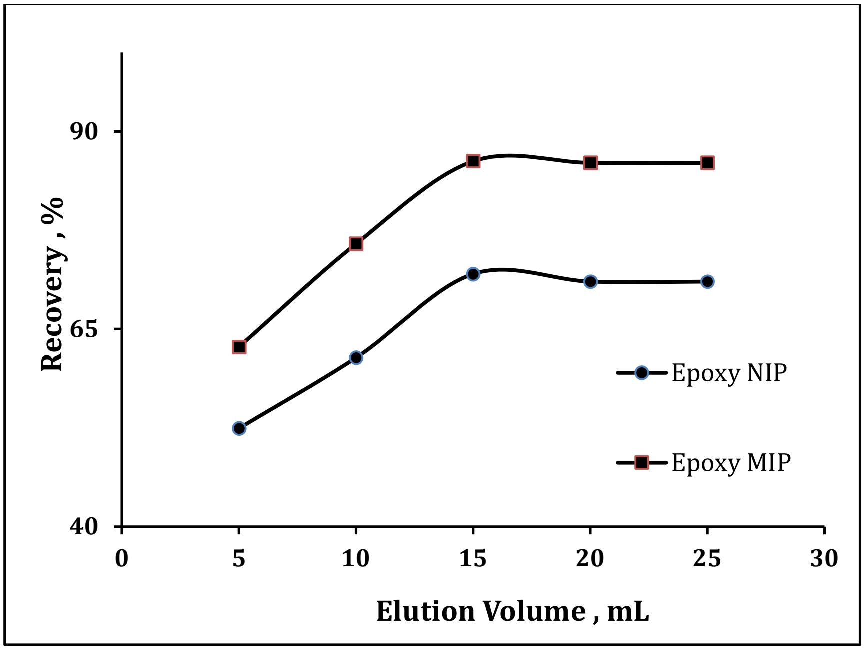

Fig.6: Effect of elution volume on the extraction recovery (%) of epoxy resin-based polymers

3.3.3 Effect of Flow Rate:

The effect of the flow rate on the extraction efficiency of methylene blue using ER-MIP and ER-NIP is shown in Fig. 7. It was evident that the extraction efficiency (%R) decreased significantly as the flow rate increased. Low flow rates allowed more contact time for dye molecules with the polymer's binding sites, leading to improved extraction efficiency through enhanced diffusion within the polymer's pores. This was the opposite at higher flow rates, as they resulted in a short contact time, leading to reduced dye diffusion and poor adsorption efficiency (Fito et al., 2023; Olorunnisola et al., 2025). Also, ER-MIP exhibited higher extraction efficiency than ER-NIP, owing to selective recognition sites within the imprinted polymers.

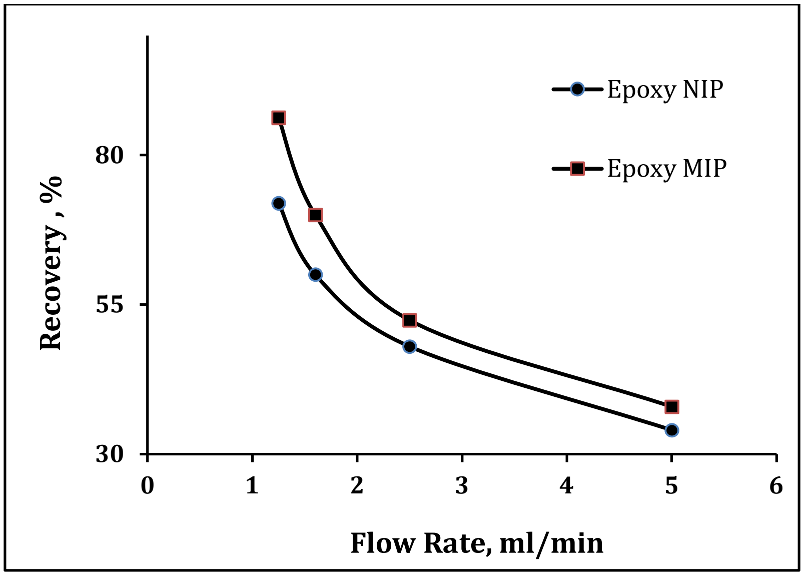

Fig.7: Effect of the Flow Rate on the Extraction Recovery (%) of Epoxy Resin-Based Polymers

3.3.4 Effect of Amount of Solid Phase:

The experimental data indicated that the increase in the amount of sorbent caused a reduction in the %R value, as shown in Fig. 8. The amount of sorbent for ER-MIP and ER-NIP systems was varied from 0.1 to 2.5 g. The optimal amount of sorbent was 0.1 g. It was seen that higher %R values were obtained with lower sorbent amounts, while an increase in the amount of sorbent decreased the %R value. This is because methylene blue molecules were strongly retained within the sorbent, preventing their desorption in the next step. Additionally, by increasing the amount of sorbent, more surface area and active sites are gained, hence promoting nonspecific adsorption, especially in ER-NIP, reducing extraction efficiency. Similar findings concerning the effect of sorbent amount on %R have been documented in previous publications in Heliyon (2021)(Maranata et al., 2021).

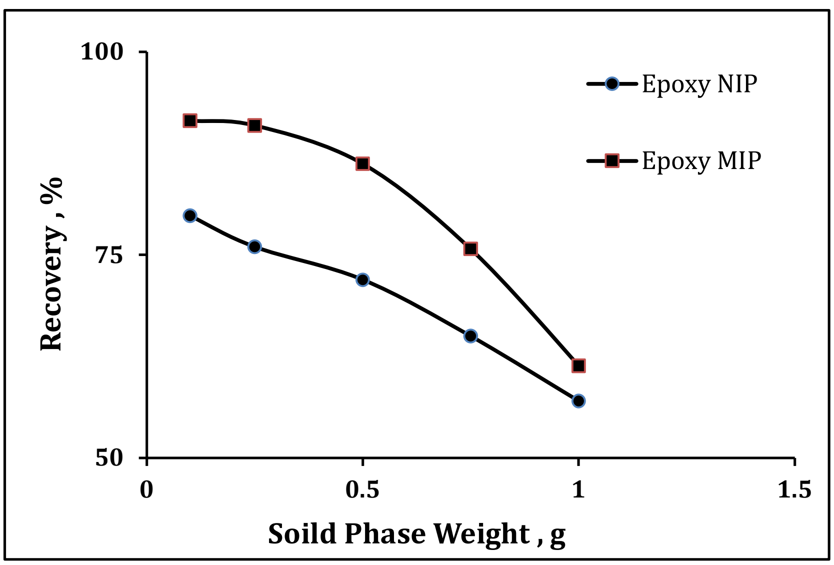

Fig.8: Effect of the Solid Phase Weight on the extraction recovery (%) of epoxy resin-based polymers

3.3.5 Effect of Dye Concentration:

The influence of dye concentration (100-500 mg/L) on the recovery percentage was evaluated using ER-MIP and ER-NIP, as shown in Fig. 9. The results indicated that the optimum recovery percentage of ER-MIP was achieved at an initial dye concentration of 100 mg/L. Further increases in dye concentration decreased recovery efficiency, possibly due to saturation of binding sites and increased competitive adsorption. In addition, ER-MIP demonstrated higher recovery percentages than ER-NIP, indicating better selectivity for methylene blue dye molecules (Al-Gorair et al., 2022).

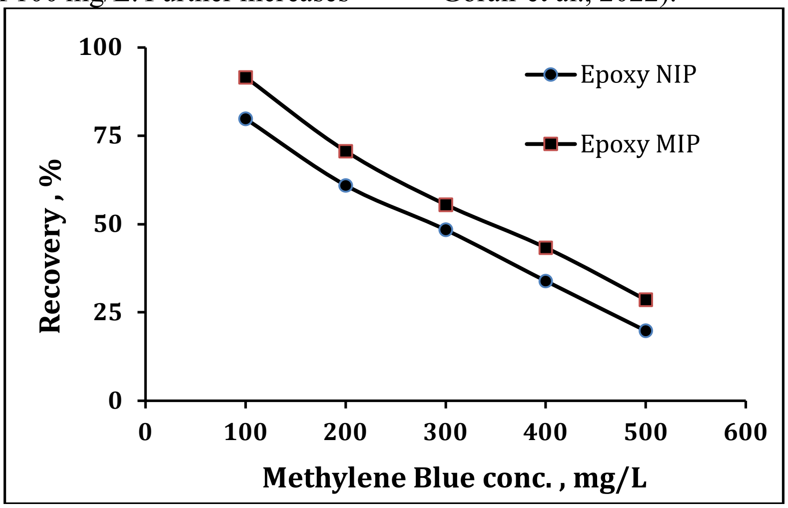

Fig. 9: Effect of Concentration on the extraction recovery (%) of epoxy resin-based polymers.

3.3.6 Effect of Dye Volume:

The effect of the volume of dye solution, 5 to 50mL, on the %R of the epoxy-based polymers was evaluated and shown in Fig. 10. The data reveal that increasing the volume of the methylene blue solution decreases the recovery percentage for both ER-MIP and ER-NIP. The high %R was observed at low solution volumes (5-15 mL) because there were sufficient binding sites relative to the dye molecules. In addition, ER-MIP displayed a higher %R than ER-NIP.

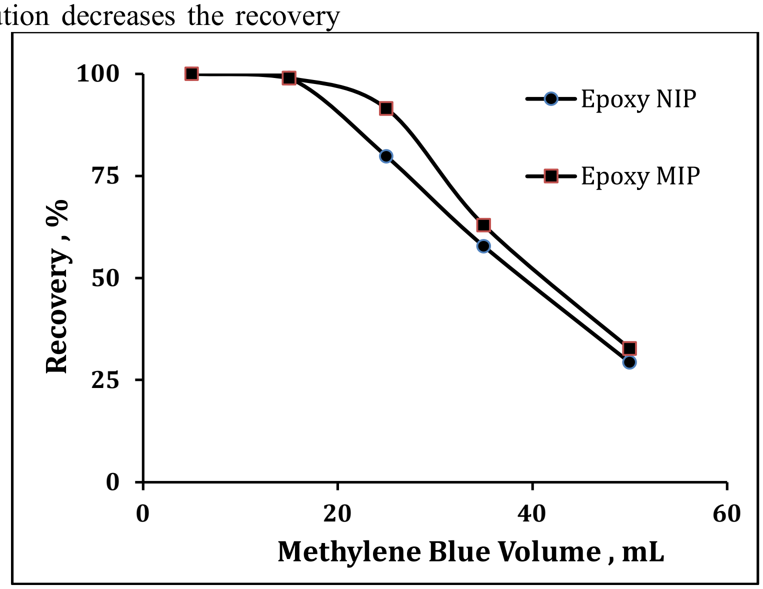

Fig.10: Effect of Dyes Volume on the extraction recovery (%) of epoxy resin-based polymers

3.3.7 Effect of pH:
The influence of pH on the extraction performance of ER-MIP and ER-NIP towards methylene blue (MB) was examined at different pH levels ranging from 2 to 12, as presented in Figure 3.35. It was found that the extraction performance progressively improved with increasing pH and peaked at pH 7–8 for both polymers.
Based on the experimental results, ER-MIP exhibited higher extraction efficiency than ER-NIP across all pH values tested, indicating that selective binding sites have been successfully synthesized on the imprinted polymer surface. Since methylene blue dye is positively charged, increasing the pH value reduces the effect of hydrogen ions in the competing adsorption process, thereby improving dye adsorption. However, at very high pH values, there was a reduction in extraction efficiency due to excess OH^- ions competing in the adsorption process (Bıyıkoğlu, 2025; Bu et al., 2025).

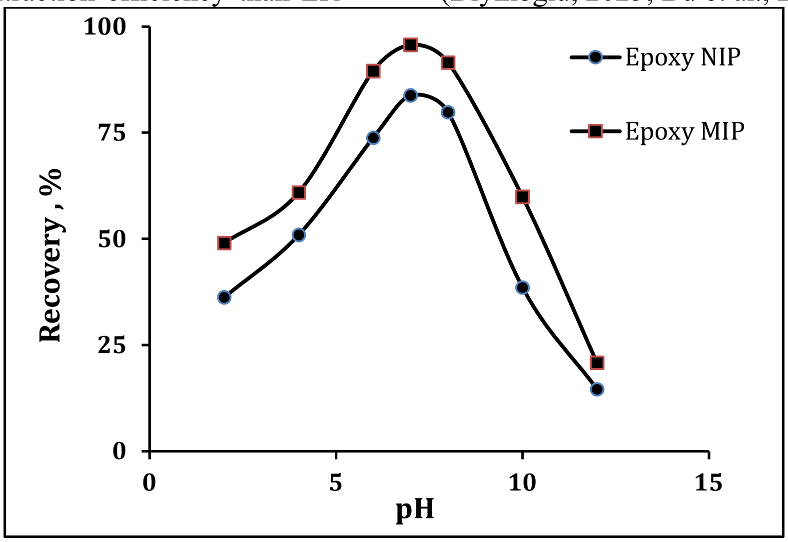

Fig.10: The Effect of pH on the extraction recovery (%) of epoxy resin -based polymers

3.4 Selectivity Evaluation:
The selectivity of the synthesized ER-MIP was compared with that of its counterpart, the ER-NIP, under optimal methylene blue (MB) extraction conditions. The adsorption performance of methylene blue was determined in the presence of interfering dyes based on Beer-Lambert's law.
In the case of binary dye systems, the absorbance of the binary system at MB's λmax and that of the interfering dye were determined. The molar absorptivity of MB and the interfering dye were calculated experimentally from the calibration graphs at both wavelengths. These values were used to analyze the concentrations of MB and the interfering dye in the binary dye system using Eq. 3 (Becskereki et al., 2021).

$$A_{total} = (\varepsilon\ b\ C)_{methylen\ \ blue} + (\varepsilon\ b\ C)_{competing\ dye} \quad \ldots..Eq.3$$

where, $A_{\ total}$ is the absorbance of the binary solution system, ε is the molar absorptivity constant, b is the optical path, and C is the dye or the competing dye concentration.

3.4.1 Removal Efficiency (%R):
The removal efficiencies of methylene blue by ER-MIP and ER-NIP were assessed by %R. A higher %R denotes a high adsorption ability of the polymer towards the dye due to a higher affinity for the target analyte. In this study, the ER-MIP shows a greater %R than the ER-NIP. This observation suggests that there is selective recognition sites created during the formation of the imprinted polymers. The presence of these sites gives the polymer an affinity towards the dye in question through complementary interactions based on size, structure, and function. The reduction in MB removal

efficiency in the presence of a competing dye indicates that the ER-MIP exhibits selectivity towards the target analyte.

3.4.2 Distribution Coefficient:

The distribution coefficient (Kd) was used to estimate the affinity of ER-MIP for methylene blue (MB) and competing dyes. The distribution coefficients were determined based on Eq. 4 (Sadia et al., 2022)

$$Kd = \frac{(c_0 - c_e)}{c_e} \times \frac{V}{m} \quad \text{.... Eq 4}$$

Where C_0 is the initial concentration, Ce is the equilibrium concentration, V is the solution volume in mL, and m is the sorbent mass in g.

The data revealed that the ER-MIP exhibited significantly higher distribution coefficients for methylene blue than for the competing dyes, indicating a greater affinity of the polymer for methylene blue. It was shown that the maximum distribution coefficient of MB was observed in the MB/TB system (4.52), whereas the competing dyes showed lower distribution coefficients (0.04-0.20). These results confirm the successful creation of selective receptors for methylene blue on the ER-MIP surface.

3.4.3 Selectivity Coefficient:

The selectivity coefficient α was determined using Eq. 5 (Mahmood et al., 2025):

$$\alpha = \frac{K_d(MB)}{K_d(Dye)} \quad \text{.... Eq. 5}$$

where K_d (MB) represents the distribution coefficient of methylene blue, while K_d (Dye) represents the distribution coefficient of the competitive dye.

The α values derived from measurements indicated the selectivity of ER-MIP for methylene blue over other dyes. The maximum α value was recorded in the MB/CR system (69.55), then MB/EBT (48.88), and lastly MB/TB (41.41). The higher values suggest that there were selective binding sites for methylene blue within the ER-MIP polymer matrix, as well as for other dyes.

3.4.4 Imprinting factor:

To determine the imprinting efficiency (IE) or selectivity of ER-MIP towards methylene blue (MB), the imprinting factor (IF) was calculated according to the following Eq .6(Luna Quinto et al., 2023a):

$$IF = \frac{K_d(MIP)}{K_d(NIP)} \quad \text{.... Eq. 6}$$

In which K_d (MIP) is the distribution coefficient of the MIP, while K_d (NIP) is the distribution coefficient of NIP.

The results showed that ER-MIP exhibited a higher IF for methylene blue than its competitors, suggesting that selective recognition sites were formed within the polymer. For MB, the IF ranged from 4.55 to 8.83, with the highest recorded for MB/TB (8.83). However, for the other competitors, the IF was very low (0.34-0.88).

Table 3: Evaluation of removal efficiency (%R), selectivity coefficients (Kd, α) and imprinting Factors (IF) for MIPs and NIPs toward methylene blue in binary dye systems.

Polymer	Binary Dye	%R		Kd		α	IF	
		MB	Dye	MB	Dye		MB	Dye
ER-MIP	MB/BG	88.95	36.03	2.01	0.14	14.29	4.55	0.84
ER-NIP		63.88	40.12	0.44	0.16	2.63		
ER-MIP	MB/TB	94.76	30.42	4.52	0.10	41.41	8.83	0.88
ER-NIP		67.21	33.04	0.51	0.12	4.15		
ER-MIP	MB/CR	92.87	15.78	3.25	0.04	69.55	8.69	0.34
ER-NIP		59.99	35.46	0.37	0.13	2.72		
ER-MIP	MB/CV	89.29	45.09	2.08	0.20	10.15	6.57	0.75
ER-NIP		55.92	52.22	0.31	0.27	1.16		
ER-MIP	MB/EBT	93.09	21.61	3.36	0.06	48.88	7.60	0.46
ER-NIP		63.92	37.24	0.44	0.14	2.98		

3.5 Methodology validation:

The proposed MISPE technique involving epoxy resin-molecularly imprinted polymer (ER-MIP) was tested by assessing the extraction recovery and selectivity for methylene blue (MB). The developed technique proved reproducible upon optimization, with a sorbent amount of 0.1 g, an elution volume of 15 mL, pH 7, and a dye concentration of 100 mg L^{-1}. UV–Vis spectroscopic measurement indicated that the determination of MB using this technique was consistent as per Beer-Lambert’s law at 664 nm. Moreover, ER-MIP demonstrated superior recovery and selectivity over ER-NIP in a binary dye mixture, with imprinting factors ranging from 4.55 to 8.83.

The efficiency removal (%R) and imprinting factor (IF) of the synthesized ER-MIP were evaluated and compared with previous studies on various dye species, as shown in Table 4. It is clear that the fabricated ER-MIP had very high adsorption efficiency and selectivity towards methylene blue.

Table 4. Comparison of the proposed approach with some references

Technique	Target Dye	%R	IF	Reference
MIP Adsorption	Basic Blue3 3	96	10.73	(Sadia et al., 2022)
Template-assisted MIP	Methyl Red	92.25	3.75	(Shafqat et al., 2023)
Magnetic MIP	Methylene Blue	95	-	(Sedelnikova et al., 2023)
MIP adsorption	Brilliant Green	High Removal Efficiency	2.35	(Luna Quinto et al., 2023b)
Fluorescence MIP Sensor	Methylene Blue	-	5.3	(Wang et al., 2020)
SPE-MIP ER-MIP)	Methylene Blue	94.76	8.83	Present Study

4. Conclusion:

The synthesized ER-MIP demonstrated high extraction efficiency, selectivity, and reproducibility for methylene blue removal from aqueous dye systems. The obtained results highlight the environmental potential of ER-MIP as a selective sorbent for dye-contaminated water treatment and wastewater remediation. Due to its selectivity, stability, and high removal efficiency, the proposed material may represent a promising environmentally relevant strategy for minimizing dye pollution and improving water quality. The high extraction efficiencies, along with a high imprinting factor, indicate the applicability of ER-MIP for dye removal.

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المعالجة البيئية للمياه الملوثة بالأصباغ باستخدام البوليمرات المطبوعة جزيئيًا القائمة على راتنج الإيبوكسي للاستخلاص الانتقائي بالطور الصلب لصبغة الميثيلين الأزرق من الأنظمة الثنائية للأصباغ

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المستخلص
في السنوات الأخيرة، أصبح تزايد تصريف مياه الصرف الصناعي المحتوية على الأصباغ مصدر قلق بيئي بالغ نظرًا لآثاره السلبية على النظم البيئية المائية وجودة المياه. في هذه الدراسة، تم بنجاح تصنيع بوليمرات مطبوعة جزيئيًا قائمة على راتنجات الإيبوكسي (ER-MIPs) وتوصيفها كمواد ماصة انتقائية لمعالجة البيئة وإزالة الميثيلين الأزرق (MB) من أنظمة الأصباغ المائية باستخدام استخلاص الطور الصلب المطبوع جزيئيًا (MISPE). استُخدم الميثيلين الأزرق كجزيء قالب لتصنيع مواقع التعرف الانتقائية القادرة على تعزيز انتقائية الاستخلاص وكفاءته في أنظمة الأصباغ الثنائية. تم تحسين العديد من المعايير التشغيلية المؤثرة على أداء الاستخلاص، بما في ذلك نوع وحجم المذيب، ومعدل التدفق، وكمية المادة الماصة، وتركيز الصبغة، وحجم العينة، ودرجة الحموضة، بشكل منهجي لزيادة كفاءة إزالة الصبغة إلى أقصى حد. تم تحقيق الظروف المثلى باستخدام مزيج من الميثانول وحمض الخليك والماء (8:1:1، حجم/حجم/حجم) كمذيب، بحجم 15 مل من المذيب، وكتلة 0.1 غرام من المادة الماصة، وتركيز 100 ملغم/لتر من الميثيلين الأزرق، ودرجة حموضة متعادلة (الأس الهيدروجيني 7). في ظل هذه الظروف، أظهر البوليمر المطبوع ER-MIP أداءً استخلاصيًا أعلى بكثير من البوليمر غير المطبوع المقابل (ER-NIP)، وذلك بفضل تكوين تجاويف التعرف الانتقائية، حيث تراوحت كفاءة الإزالة بين 89.13% و94.76%، ومعاملات الطباعة بين 4.55 و8.83. تُظهر هذه النتائج إمكانية تطبيق البوليمرات المطبوعة ER-MIP كمواد ماصة انتقائية وفعالة وصديقة للبيئة لمعالجة المياه الملوثة بالأصباغ ومعالجة مياه الصرف الصحي.
الكلمات المفتاحية: Molecularly imprinted polymers (MIPs)، الميثيلين الأزرق، الاستخلاص بالطور الصلب، Epoxy resin، المعالجة البيئية.