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A NEW MIP EMBEDDED CRYOGEL FOR SELECTIVE PRE-CONCENTRATION AND REMOVAL OF PROPACHLOR

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ABSTRACT

Propachlor is a pesticide commonly used in the chloroacetanilide herbicide group. Propachlor contamination occurs in groundwater resources and soil sources. Therefore, removal and also the determination of trace amounts of propachlor is a very important issue. Molecularly imprinted polymers (MIPS) are preferred for their advantages such as high affinity, strength, and selectivity in pesticide removal and determination. In this study, MIP embedded cryogel was synthesized for selective adsorption and removal of propachlor. MIP synthesis was performed using the template molecule propachlor, functional monomer methacrylic acid (MAA), crosslinker ethylene glycol dimethacrylate (EDGMA), solvent hexadecane and 2,2-azo-bis-isobutyronitrile (AIBN) as the initiator. Cryogels are a good alternative for separation and purification because of their advantageous properties such as short diffusion, low pressure and adsorption and elution in a short time. The structure of MIP was determined using scanning electron microscopy (SEM), Elemental analysis and Fourier transform infrared spectroscopy (FT-IR), and the structure of MIP embedded cryogel was determined using scanning electron microscopy (SEM). The highest adsorption capacity for MIP embedded cryogel was found to be 14.38 mg g^{-1}. The obtained sorbent was selective for propachlor according to other similar pesticides. MIP embedded cryogel was used for selective preconcentration of propachlor in environmental samples and as a result, high recovery values were achieved in the preconcentration (%80-%98) The concentration of propachlor in environmental samples was analyzed by high-performance liquid chromatography (HPLC).

Keywords: Propachlor, Adsorption, Molecular imprinting, Cryogel

1. INTRODUCTION

Herbicides are phytotoxic chemicals used for destroying various weeds or inhibiting their growth. Chloroacetanilide herbicides exhibit broad-spectrum pre- and early post-emergence control of most grasses and broad-leaved weeds in a wide variety of agro-economically important crops. Propachlor (2-chloro-N-isopropyl-acetanilide) has been extensively employed for the protection of corn, sorghum, soybeans and a variety of vegetables [1], [2]. Propachlor can easily transfer to soil systems because of its high water solubility (700 mg L^{-1}) [3]. As with many other herbicides, propachlor has harmful effects on animals. Propachlor may produce slight development or adverse reproductive effects. It is not genotoxic or clastogenic in mammals. However, there is evidence that it produces benign hepatic tumors in mice [4]. For these reasons, removal and determination of trace levels of propachlor are important issues for the protection of the environment. Limited studies have been carried out in the literature for this purpose. Some of these studies include mineralization of propachlor by electrochemical [3] or bacterial route [5], while others involve removal by adsorption. In Tuzimski and friends' study; 21 pesticides belonging to different chemical classes were extracted with liquid-liquid partitioning with acetonitrile followed by dispersive solid-phase extraction using zirconia-coated silica particles and analyzed using high-performance liquid chromatography with diode-array detection (HPLC–DAD). The recovery values for most of the studied pesticides for extra virgin olive oil and grape seed oil samples ranged from 50% to 130% and the analysis of pesticide residues was realized at the level of ng g^{-1} of edible oil samples [6]. This study is no selective for propachlor. Konstantinaou and friends were used Al-pillared and Fe-Al-pillared clays and mesoporous alumina aluminum phosphates for adsorption and removal of propachlor and some herbicides. In this study, the obtained recovery range is only %60.9 for

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propachlor [1]. In the other study, the molecularly imprinted polymers (MIPs) were used as the base material of solid-phase extraction (SPE) for the separation and pre-concentration of the propachlor herbicide in the different environmental matrix. Concentrations of propachlor in the samples were analyzed by high-performance liquid chromatography [7]. This study is selective for propachlor adsorption. On the other hand, the obtained adsorption capacity values are not high enough.

Molecular imprinting is a technology to create recognition sites in a macromolecular matrix using a molecular template. Target molecules (i.e., propachlor) can be used as templates in cross-linked polymers. After the removal of the template, the remaining polymer seems to be more selective [8], [9]. Molecularly imprinted polymers can be used as a solid-phase material in many areas, especially as a sorbent for the selective adsorption of herbicides [10]–[12]. In this study, MAA, which is frequently used in the literature as a monomer [13], [14], was preferred for MIP synthesis.

Cryogels are very good alternatives to separation and purification with many advantages such as large pores, short diffusion path, low-pressure drop and very short times for both adsorption and elution [15], [16].

In this study, these advantages of cryogels have been combined with the selectivity of molecularly imprinted polymers (MIP) and a new sorbent was synthesized for propachlor. MIP embedded cryogel has been used for selective adsorption and pre-concentration of propachlor from some environmental samples like such as corn and puddles in the agricultural land.

2. MATERIALS and METHODS

2.1. Materials

Propachlor, methanol, metolachlor, acetanilide, Hydroxyethyl methacrylate (HEMA), ammonium persulfate (APS) were bought from Sigma – Aldrich. Methacrylic acid (MAA) and sodium dodecyl sulfate (SDS) were supplied by Alfa Aesar. Ethylene glycol dimethacrylate (EGDMA), azobisisobutyronitrile (AIBN), glycine, N, N'- Methylene bisacrylamide (MBAAm), N, N, N', N'-Tetramethylethylenediamine (TEMED) were supplied by Fluka. N-Hexadecane, potassium dihydrogen phosphate (KH_2PO_4), hydrogen chloride (HCI), sodium chloride (NaCI) were supplied by Merck. Potassium hydroxide (KOH) was supplied by Riedel-de Haën.

2.2. Methods

2.2.1. Synthesis of propachlor imprinted polymer

For the synthesis of propachlor imprinted polymer; 0.245 mmol propachlor, 0.84 mmol MAA and 3.4 μmol EDMA were dissolved in 0.34 mmol of hexadecane. The dispersion medium was prepared by dissolving 0.0192 g sodium dodecyl sulfate in 9 mL of water. After the AIBN addition to the first solution, this solution was transferred into the dispersion medium by using a homogenizer. The obtained solution was stirred at 70^0C for 24 h in a thermostatic water bath. After polymerization, the formed MIPs were separated from the polymerization medium. The residuals (e.g., unconverted monomer, initiator, and solvent) were removed by an extensive cleaning procedure with methanol and water. To form the template, the synthesized polymer was treated with methanolic KOH at 70^0C for 24 h in a thermostatic water bath.

2.2.2. Synthesis of MIP embedded cryogel

For this purpose; 0.260 ml HEMA was used as the monomer. Then, 0.37 mmol of N, N'-Methylenebisacrylamide (MBAAm) and 0.024mmol MIP were added into 4.74 ml deionized water as a crosslinker agent. HEMA, MIP and crosslinker agent were mixed and stirred about 20 minutes at room temperature. Then, the mixture was put in an ice bath and cooled. Then 0.017 mmol APS and 0.033 mmol TEMED added into the solution quickly as redox initiator pairs. After that mixture was poured into a plastic syringe and frozen at -20 °C during 18 h. After the freezing process, the syringe was put at room temperature for the thawing process. At the end of thawing, gel matrices occur. Cryogel was washed deionized water 3 times to remove unreacted soluble materials. A blank cryogel was prepared in the same way without MIP. Cryogels were kept in a 0.02 % sodium azide solution until use.

2.2.3. Characterization of MIP and MIP embedded cryogel

Elemental analysis of unleached (before washing with KOH) and leached (after washing with KOH) MIP microbeads was carried out by using Leco, CHNS-932, ABD Elemental Analysis System. For analysis, 1 mg of MIP was weighted at ±0.0001 g sensitivity and put into the system.

FT-IR spectra of unleached (before washing with KOH) and leached (after washing with KOH) MIP were obtained by FT-IR spectrophotometer (Perkin Elmer Model 2000). The dry sample (about 0.1 g) was thoroughly mixed with KBr (0.1 g, IR Grade, Merck, Germany), and pressed into a pellet form and the FT-IR spectra were then recorded.

The morphology of the dried cryogels and propachlor imprinted polymer were investigated by using Leo S 440 model scanning electron microscope.

The swelling ratio of cryogel was determined in distilled water. Initially, the cryogel sample was washed until the washing was clear. Then it was dried to constant mass, the mass of the dried sample was weighed (±0.0001 g). This dried sample was being placed into the swelling medium at room temperature for 24 h. Then the mass of the wet sample was determined by weighing. The swelling ratio was calculated by using the following expression (Eq 1):

$$Swelling\ ratio\ \% = \left[\frac{W_s - W_0}{W_0}\right] x100 \qquad (Eq\ 1)$$

where W_0 and W_s are the weights of cryogels before and after swelling, respectively.

2.2.4. Equilibrium binding analyses and selectivity studies

The adsorption capacity of the MIP embedded cryogel and blank cryogel for propachlor were determined in the batch model. The adsorption capacity of MIP embedded cryogel was determined with propachlor standard solutions at different concentrations. For the determining of propachlor adsorption capacity of cryogels, the cryogels were washed with 50 ml of water and then equilibrated with 25 mM phosphate buffer. Then, propachlor solution was pumped through the column by a peristaltic pump. The total concentration of propachlor was determined spectrophotometrically at 210 nm by using a UV–vis diode array spectrophotometer in all adsorption studies. The adsorption capacity was calculated from the following expression (Eq 2):

$$Q = \frac{(C_0 - C)xV}{m} \qquad (Eq\ 2)$$

where Q is the amount of propachlor adsorbed onto the unit mass of cryogel (mg g^{-1}), C_o and C the concentration of the propachlor in the initial solution and the aqueous phase after adsorption, respectively (mg ml^{-1}), V the volume of the aqueous solution (ml) and m is the mass of the dried cryogel. The experiments were performed in replicates of three and the sample was analyzed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean value and standard deviations. Confidence intervals of 95% were calculated for each set of samples in order to determine the margin error.

To optimization of adsorption of the propachlor, some parameters like pH, initial concentration, duration of interaction and flow rate effects were evaluated. Desorption of adsorbed propachlor was tried by using different eluents like methanol, methanol-water, 0.1 M NaOH solution. At the end of these studies, methanol was selected as a regeneration reagent. The binding interaction and equilibrium information between the MIP embedded cryogel and propachlor can be obtained by Scatchard analysis. This analysis employs Eq. (3):

$$\frac{Q}{C} = \frac{Q_{max}}{K_D} - \frac{Q}{K_D} \qquad (Eq\ 3)$$

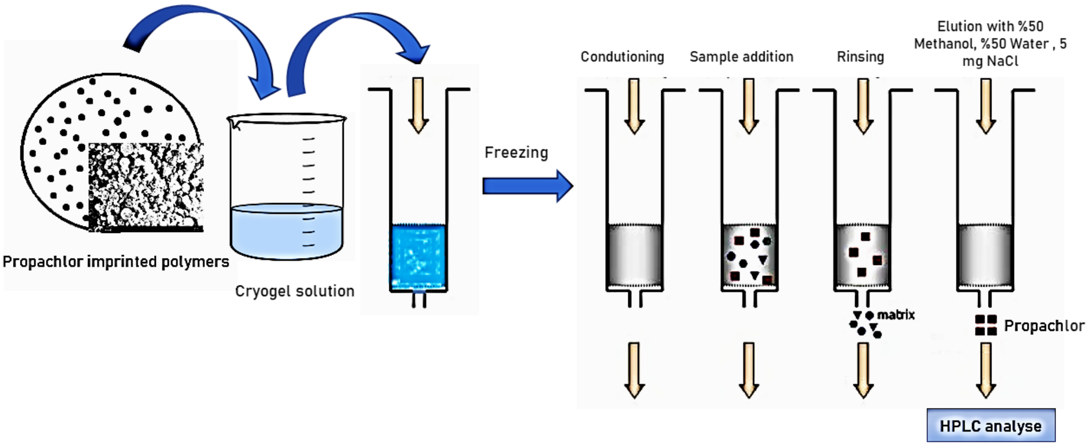
where Q is the amount of propachlor bound to the cryogel, as calculated by the UV–vis variation upon addition of analyte and C is the concentration of free propachlor. Qmax represents the apparent maximum number of binding sites, and K_D is the equilibrium dissociation constant of the cryogel. The selectivity of MIP embedded cryogel for propachlor which is a chloroacetanilide was estimated by using acetanilide and metolachlor. For this purpose, calibration charts were created using UV-vis for each substance (at 210 nm). The selectivity coefficient for the binding of propachlor in the presence of competitor species can be obtained from equilibrium binding data according to Eq. (4):

$$k = \frac{Q_{\max(prop)}}{Q_{\max(X)}} \qquad (Eq\ 4)$$

where k signifies the selectivity coefficient and X represents competitor species.
A comparison of the k values of the imprinted polymer with those molecules allows an estimation of the effect of imprinting on selectivity.

2.2.5. Application of the method to real samples

Water samples obtained from puddles in the agriculture land (Keskin Town, Eskişehir) and fresh corn were used as real samples. No pretreatment was applied to water samples. It was only filtered and spiked with standard propachlor solutions. Dried fresh corns (3g) were mixed with 30 mL methanol for 1 day. Then the solution was filtered with a membrane filter and spiked with standard propachlor solutions. Concentrations of propachlor in water and corn samples were analyzed using HPLC (Agilent 1100 series) and UV detection under the following conditions: Inertsil ODS-3 (4,6x150 mm) column, mobile phase methanol/water (70/30, v/v), at wavelength of 220 nm, at 1.0 mL/min and room temperature. In these conditions, the propachlor peak was eluted at 4.3 minutes (t_R). The working range of the obtained calibration graph is 0.106-100 ppm of propachlor. Each analysis was repeated in triplicate. Also, LOD and LOQ of this analysis were obtained as 0.035 and 0.106 ppm, respectively.
A flowchart about the experimental methodology for this study was given in Schema 1.



Schema 1. Flowchart of experimental methodology

3. 3. RESULT AND DISCUSSION

3.1. Characterization of MIP and PHEMA-MAPA Cryogel

The elemental analysis results showed that the MIP contains 56.26% C; 10.42% H and 0.273% N before the removal of the target molecule, propachlor. After target removal, the elemental composition of MIP stood at 58.77% C; 7.384 % H and 0.069% N. The increasing ratio of C and decreasing ratio of N show the removal of the target because there is nitrogen in the propachlor structure. Additionally, the difference of IR spectra of before and after removal of propachlor from MIPs has confirmed the formation of the template (Figure 1). As seen from Figure 1, the O-H stretching of the hydroxyl bonds which became free when the propachlor was removed from the polymer became apparent at 3435 cm^{-1}.

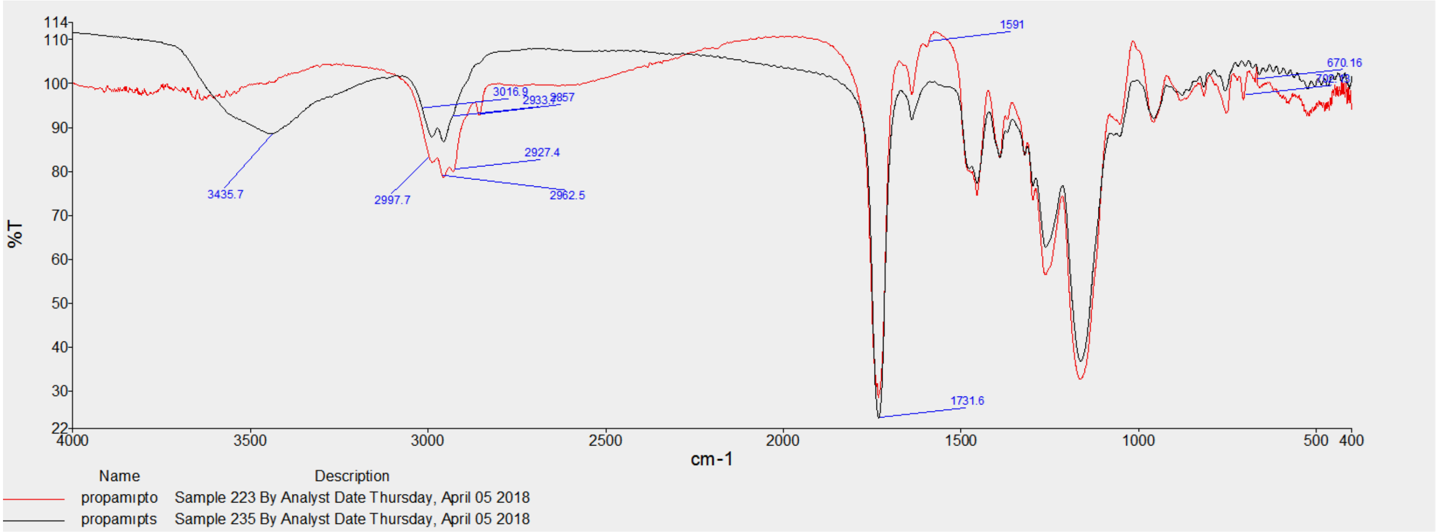


Figure 1. IR spectra of propachlor imprinted polymer, before and after template removal.

The equilibrium swelling test results were found as 11.86 g water/g cryogel and 12.69 g water/g cryogel for MIP embedded cryogel and blank cryogel, respectively.

The morphology of these two types of cryogels and MIP were investigated by scanning electron microscope (SEM). As seen from Figure 2, the synthesized MIP are nanoparticles at about 200 nm diameter. Blank cryogel and MIP embedded cryogel have large pores. In the SEM images of MIP embedded cryogel; the MIP nanoparticles are covered in the walls of the cryogel.

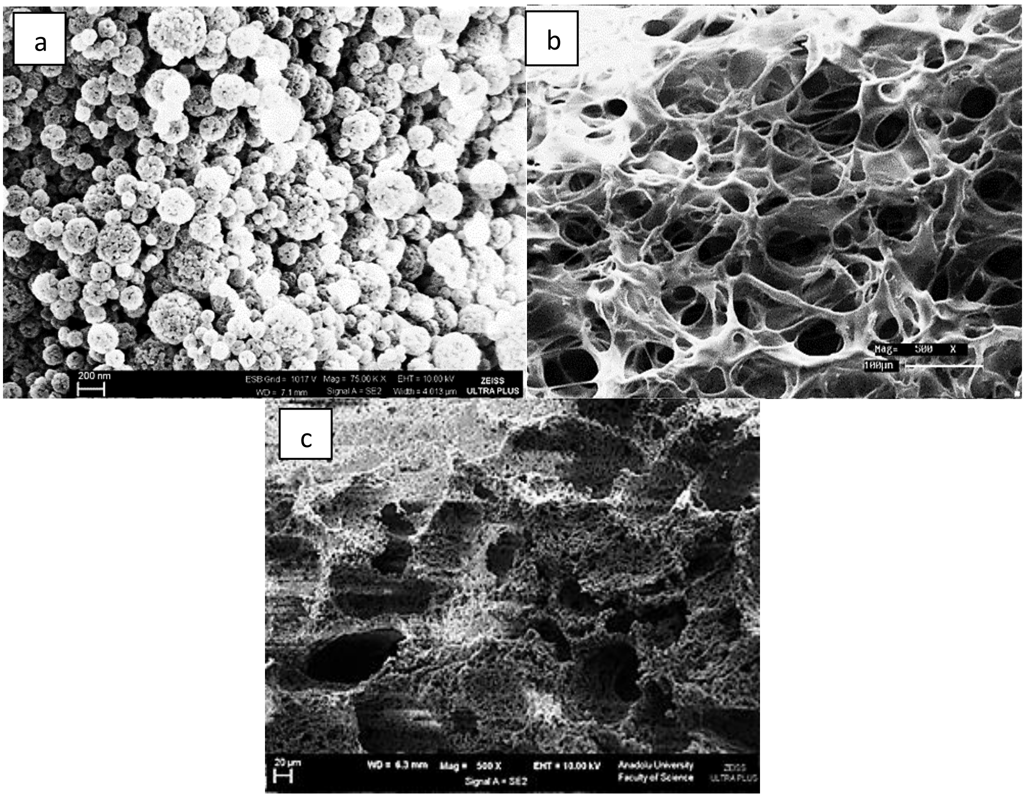


Figure 2. SEM images of (a) propachlor imprinted polymer (b) blank cryogel (c) MIP embedded cryogel

3.2. Adsorption of Propachlor from Aqueous Solution by MIP

The effectiveness of the adsorption of an analyte onto the sorbent depends significantly on pH. The effect of pH on the propachlor adsorption of the prepared MIP was investigated using HCl, NaOH, and phosphate buffer solutions (pH 6.0–8.0) containing 15 ppm propachlor. The results were given in Figure 3. The highest adsorption capacity was observed at pH 5.0 as 5.58 mg g^{-1}. This change due to pH is due to the carboxyl acid groups in the polymer matrix. pKa value of polymethacrylic acid is 4.8. Protanation at low pHs and deprotanization at high pH disrupts the noncovalent bonds between polymer and analyte [17]. According to this result, all experiments related to adsorption capacity have been carried out in a neutral and aqueous medium without adjusting of pH. This situation provides easiness during the study.

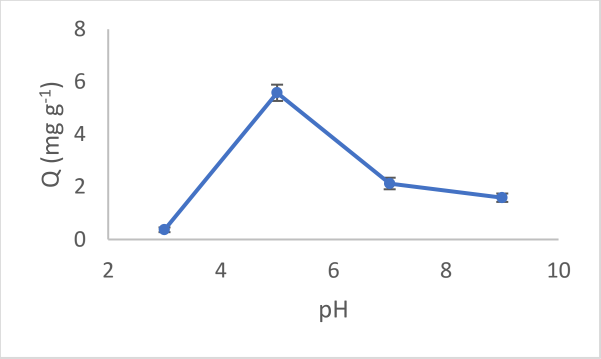


Figure 3. Effect of pH on adsorption of propachlor to MIP, propachlor initial concentration: 15 mgL^{-1}; T: 25°C; interaction time:1 h.

For the investigation of the effect of the initial concentration on the adsorption of propachlor, the MIP polymer interacted with propachlor solutions at different concentrations. As seen in Figure 4a, the adsorption capacity increased with increasing concentration of propachlor and saturation was observed when the initial concentration value reached to 30 mg L^{-1} (0.14 mM). The maximum adsorption capacity was found to be 7.46 mg g^{-1}.

Also, the effect of interaction time on the propachlor adsorption of the prepared MIP was investigated. For this purpose, 15 ppm propachlor solution interacted with MIP sorbent in different periods (5–180 min). As seen in Figure 4b, the adsorption of propachlor was completed in 60 min and reached saturation.

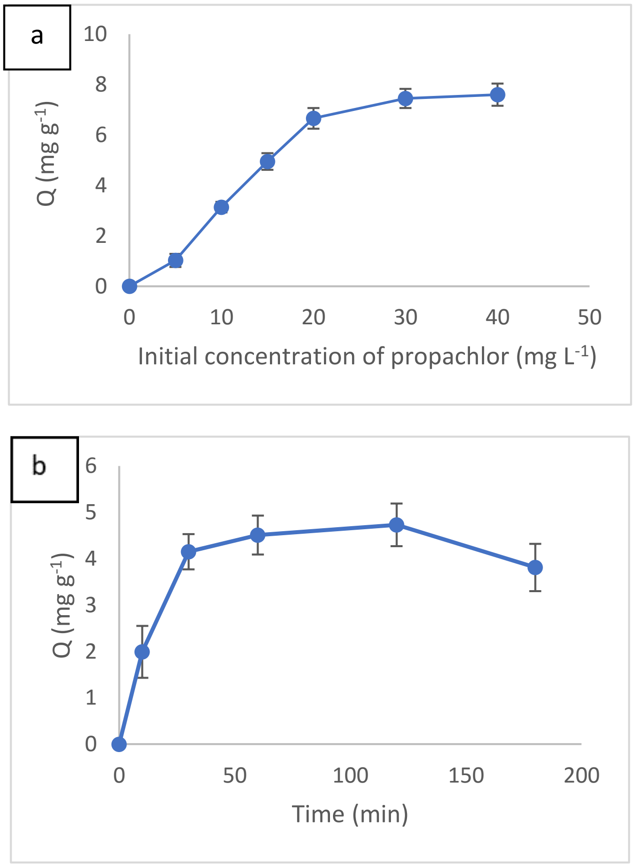


Figure 4. Effect of a) initial concentration on adsorption of propachlor to MIP; T: 25°C; interaction time:1 h. b) interaction time on adsorption of propachlor to MIP; propachlor initial concentration: 15 mg L^{-1}; T: 25°C; pH:5,

3.3. Adsorption of Propachlor from Aqueous Solution by MIP Embedded Cryogel

The effect of the initial concentration of propachlor on the adsorption of propachlor was investigated for MIP embedded cryogel. As seen in Figure 5, the adsorption capacity increased with increasing concentration of propachlor and saturation was observed when the initial concentration value reached to 30 mg L^{-1} (0.14 mM). The maximum adsorption capacity was found to be 14.38 mg g^{-1}. This value is higher than the adsorption capacity of MIP in this study (7.46 mg g^{-1}) and also literature; Rong Qu and coworkers found the maximum adsorption capacity of propachlor as about 10 mg g^{-1} when they used 2 mM initial concentration of propachlor and MIP modified silica gel [7].

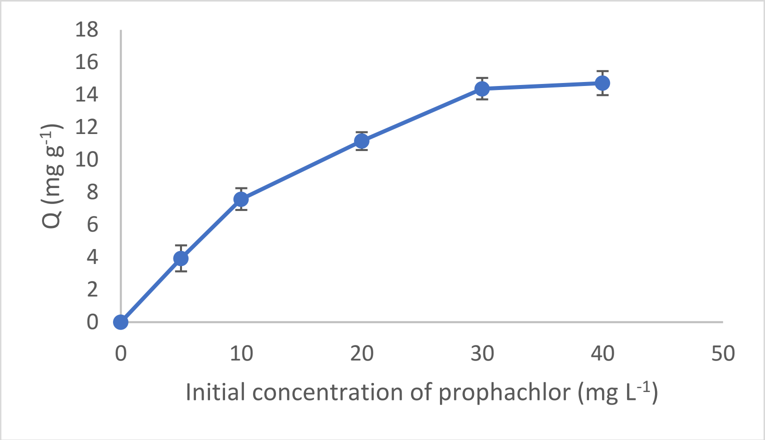


Figure 5. Effect of initial concentration on adsorption of propachlor to MIP embedded cryogel

When adsorption data of propachlor were fitted against Langmuir and Freundlich isotherms, satisfactory fits were found with the Langmuir isotherm. The Langmuir isotherm is valid monolayer sorption on a surface containing a finite number of binding sites [18]. The R^2 value of Langmuir plot and Freundlich plot were found to be 0.9916 and 0.942 respectively (Figure 6)

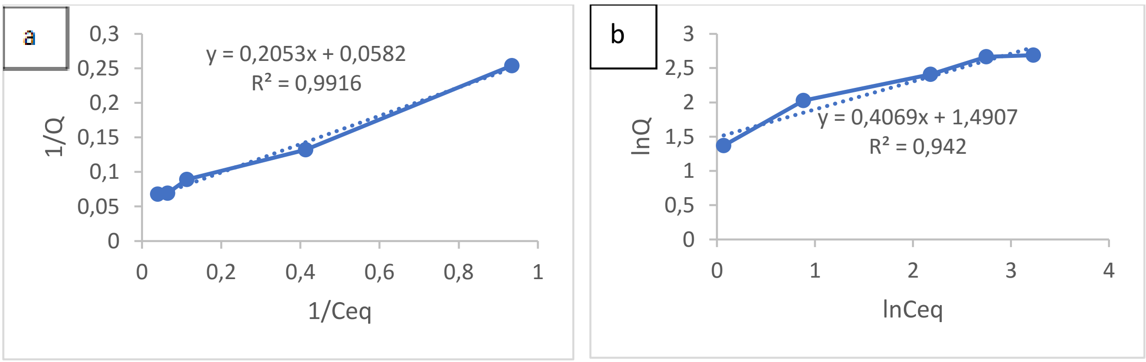


Figure 6. a) Langmuir, b) Freundlich Adsorption isotherms of MIP embedded cryogel

The association constant (Ka) for the specific interaction between the cryogel and the template (propachlor) itself was determined by Scatchard's plots using MIP embedded cryogel. (Figure 7)

The Ka for the binding of propachlor to MIP embedded cryogel is 7.90×10^3 M^{-1} and the maximum number of ligand-exchange interaction sites, Qmax, is 26.15 mg g^{-1}.

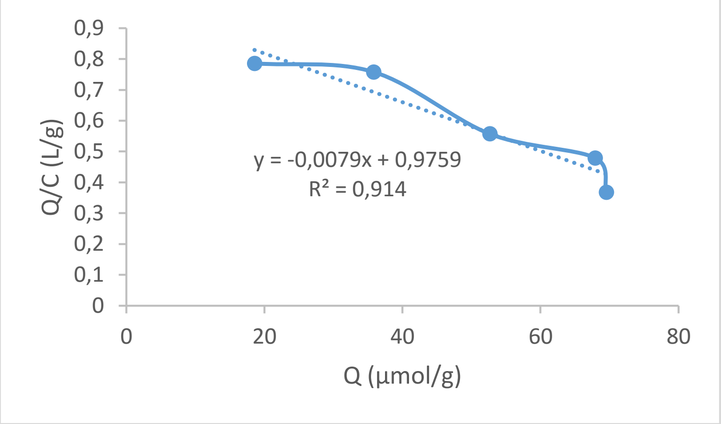


Figure 7. Scatchard plots of propachlor rebinding by the MIP embedded cryogel

The effect of flow rate on adsorption on cryogel was investigated. For this purpose 20 ppm propachlor solution was passed through the column at different speeds (0.1, 0.2 and 0.4 mL min^{-1}) After each measurement, the column was regenerated by washing with methanol: water and NaCl mixture. The adsorption capacities at different flow-rates are given in Figure 8. As seen from Figure 8 the adsorption capacity decreased as the flow rate increased. The optimum flow rate was chosen as 0.2 ml min^{-1} because there is not much difference in adsorption capacities with 0.1 ml min^{-1} and it is faster.

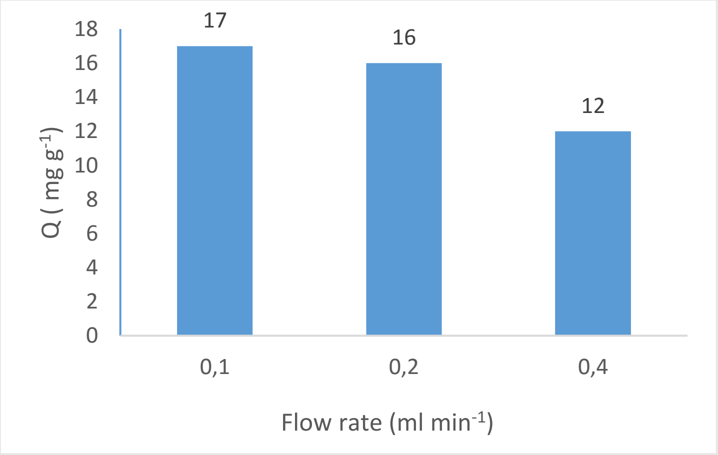


Figure 8. The adsorption capacities at different flow-rates

3.4. Selectivity Studies

The selectivity of the prepared cryogels was investigated by using metolachlor and acetanilide instead of propachlor in the adsorption studies. Metolachlor is another chloroacetanilide pesticide and their structure are very similar to propachlor. Acetanilide is smaller than these molecules. The molecular structures of acetanilide, metolachlor and propachlor were given in Figure 9. In all selectivity studies, equal concentration (10 ppm) of solutions and the same flow rate (0.2 ml min^{-1}) was used. According to experiments, the Qmax values of propachlor, metolachlor, and acetanilide were determined as 9.65 mg g^{-1}, 7.58 mg g^{-1} and 2,83 respectively, when MIP embedded cryogel was used. This is related to the selectivity of the cavity obtained in MIP. The same experiments were realized by using blank cryogel. As seen in Figure 9, there is no significant difference in adsorption amounts was observed. There is only non-selective adsorption that occurs in the pores of the cryogel. The obtained selectivity coefficients of propachlor imprinted polymer embedded cryogel were given in Table 1.

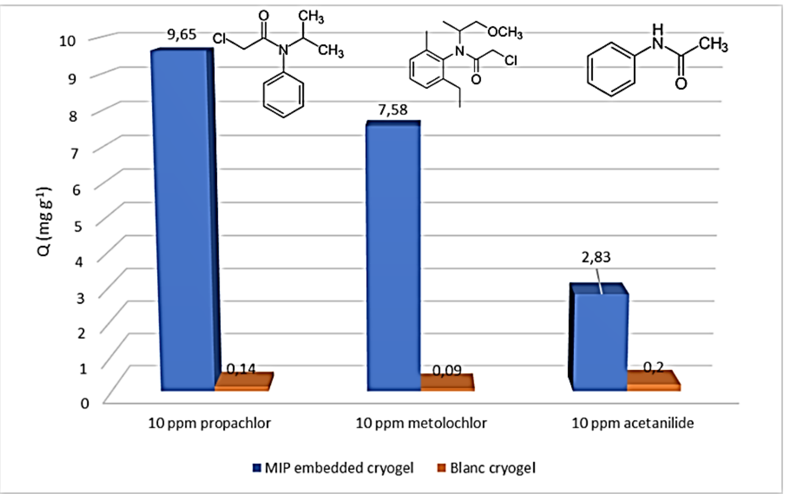


Figure 9. Effect of imprinting on selectivity

Table 1. Selectivity coefficients of propachlor imprinted polymer embedded cryogel

	Q(mg/g) (MIP embedded cryo)	**α($Q_{propachlor}/Q_{other}$)**
Propachlor	9.65	1
Metalochlor	7.58	1.27
Acetanilide	2.83	3.40

3.5. Reusability and Stability of the MIP Embedded Cryogel

In order to show the stability and reusability of the cryogel, the adsorption-desorption cycle was repeated 15 times using the same cryogel. But firstly, some experiments have been done to find the ideal regeneration solution. The tried solutions and the results obtained at this stage are given in Table 2. As can be seen in the table, the highest desorption was obtained when 100% methanol was used. However, methanol damaged the cryogel when used alone. Therefore, it was mixed with water. In this case, the amount of desorption decreased. This problem was solved by adding NaCl to the methanol-water mixture and this mixture was chosen as appropriate desorption eluent.

For sterilization after one adsorption experiment, the cryogel was washed with desorption eluent for 10 min and then distilled water for 15 min at 0.2 ml min^{-1} flow rate. As seen in Figure 10, the cryogel is very stable and can be used at least 15 times without a significant decrease (%3) in its capacity.

Table 2. The desorption eluents used for regeneration of cryogel

Desorption Eluent	**Desorption ratio,%**
%100 Methanol	100 %
%100 Ethanol	92 %
Glycine-HCl	54 %
%50 Methanol, %50 Water	53 %
%50 Methanol, %50 Water , 5 mg NaCl	100 %

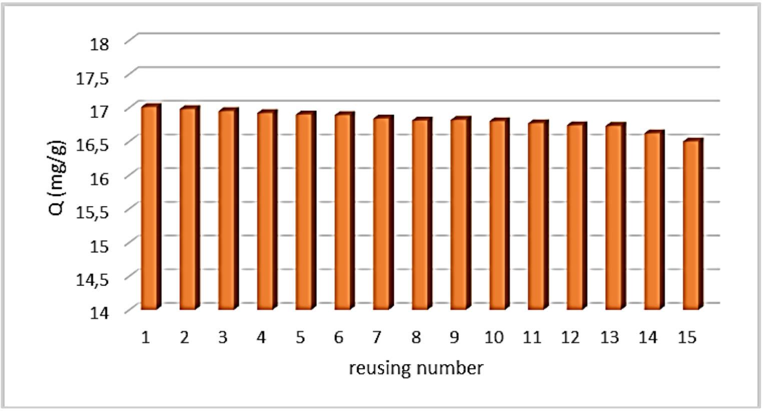


Figure 10. Reusability of MIP embedded cryogel

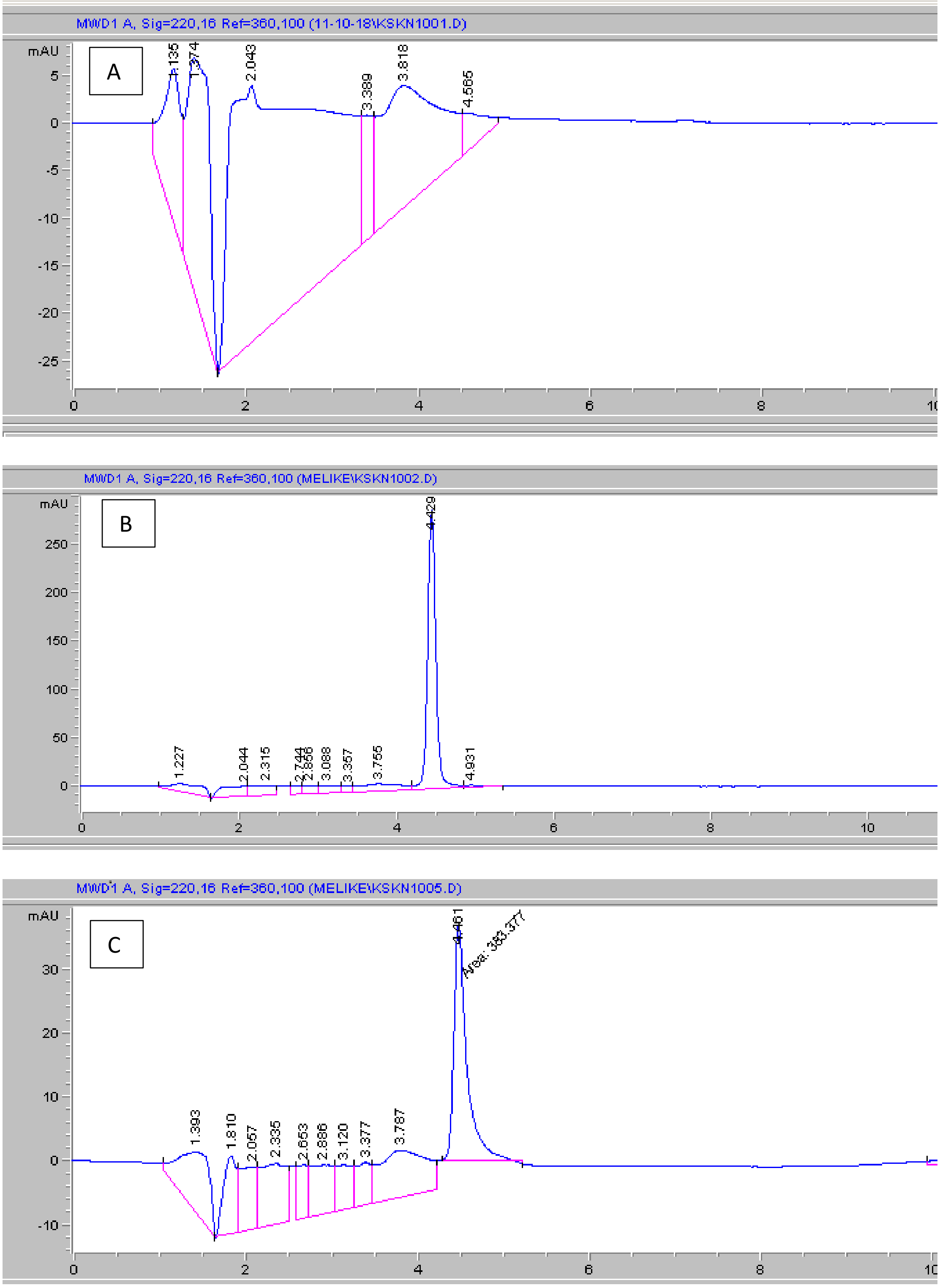
3.4. Testing of Real Samples with MIP Embedded Cryogel

The water and corn samples were spiked with propachlor standard solution at 10, 25 and 50 mg L^{-1}, respectively. Firstly, spiked samples were analyzed with HPLC. Then these samples were treated with MIP embedded cryogel column and eluates analyze with HPLC. Finally, MIP embedded cryogel was washed with 2:2 methanol: water includes 5 mg NaCl for desorption and regeneration. And these eluates were also analyzed with HPLC. Chromatograms obtained for the water sample are given in Figure 11 as examples. As seen from Figure 11 A, in the chromatogram of the water sample (puddle), the peak of propachlor could not be observed. Therefore, spiked samples were studied.

The average recoveries of the spiked samples were 68-82 % (RSD, 3.08-5.86%) for water and 86-99% (RSD, 2.25-5.36%) for corn samples. All recovery results were given in Table 3. When these values are compared with the literature [1], it can be said that good recoveries are obtained especially for corn samples.

Table 3. Recovery values of propachlor from spiked water and corn samples

Samples	Spiked concentration (mg l^{-1})	Recovery (%)			Average recovery (%)	RSD (% n=3)
		1	2	3		
Water	10	72.02	66.94	64.20	67.72	5.86
	25	77.14	80.16	82.44	79.91	3.33
	50	81.14	79.65	84.56	81.78	3.08
Corn	10	86.57	90.59	94.80	90.65	4.53
	25	100.65	96.42	99.75	98.94	2.25
	50	90.64	86.35	81.41	86.12	5.36


MWD1 A, Sig=220,16 Ref=360,100 (11-10-18\KSKN1001.D)
A
mAU
5
0
-5
-10
-15
-20
-25
1.135
1.374
2.043
3.389
3.818
4.565
0
2
4
6
8
10
MWD1 A, Sig=220,16 Ref=360,100 (MELIKE\KSKN1002.D)
B
mAU
250
200
150
100
50
0
1.227
2.044
2.315
2.744
2.856
3.088
3.357
3.755
4.429
4.931
0
2
4
6
8
10
MWD1 A, Sig=220,16 Ref=360,100 (MELIKE\KSKN1005.D)
C
mAU
30
20
10
0
-10
4.461
Area: 383.377
1.393
1.810
2.057
2.335
2.653
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3.377
3.787
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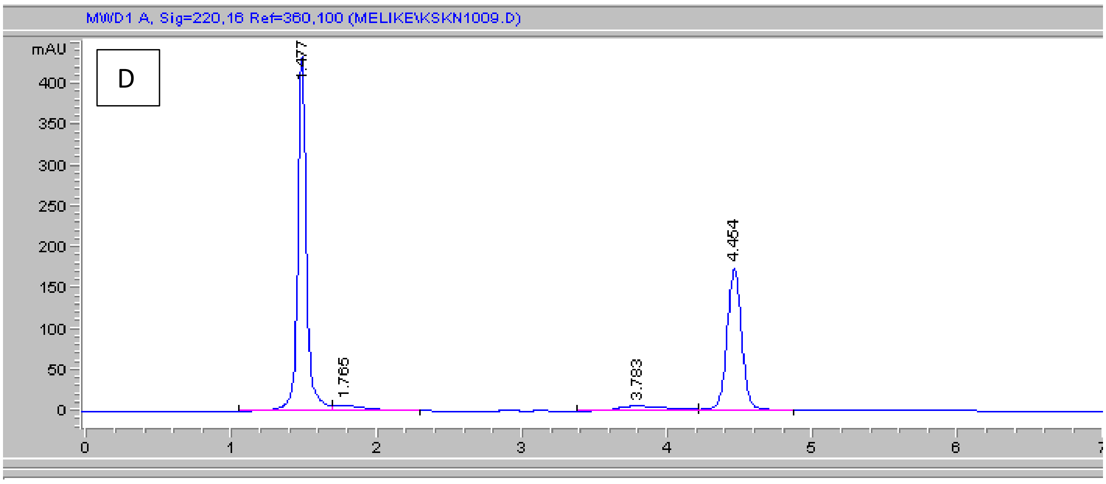

Figure 11 Chromatograms of (A)Keskin Town water sample, (B) propachlor spiked water sample, (C) eluate obtained from MIP embedded cryogel, (D) pre-concentrated spiked water sample (desorption was realized with 2:2 methanol: water includes 5 mg NaCl)

4. CONCLUSION

In this study, we have developed a new solid-phase extraction material, for selective pre-concentration of propachlor. For this purpose, we benefited from the selectivity and stability of MIP and porosity and flexibility of cryogels. The new MIP embedded cryogel material was tested for the pre-concentration of propachlor in real samples. Propachlor was not found in puddles and corn samples obtained from Keskin region of Eskişehir province. Also, prepared croyogel was tested for the preconcentration of propachlor by the standard addition method. As a result, the prepared column can be used repeatedly and easily for selective propachlor adsorption and desorption. Also, the recovery values obtained are quite good compared to the literature. It has been seen that this prepared solid-phase extraction column can be used effectively in removing the harmful pesticide, propachlor, as well as preconcentration.

REFERENCES

[1] Konstantinou IK, Albanis TA, Petrakis DE and Pomonis PJ, Removal of herbicides from aqueous solutions by adsorption on Al-pillared clays, Fe–Al pillared clays and mesoporous alumina aluminum phosphates, Water Res., vol. 34, no. 12, pp. 3123–3136, Aug. 2000.

[2] Muñoz A. *et al.*, Studies on the atmospheric fate of propachlor (2-chloro-N-isopropylacetanilide) in the gas-phase, Atmos. Environ., vol. 49, pp. 33–40, Mar. 2012.

[3] Gençten M and Özcan A. A detailed investigation on electro-Fenton treatment of propachlor: Mineralization kinetic and degradation intermediates, Chemosphere, vol. 136, pp. 167–173, Oct. 2015.

[4] Gupta PK. Toxicity of herbicides, in Veterinary Toxicology, Elsevier, 2012, pp. 631–652.

[5] Martin M, Mengs G, Plaza E, Garbi C, Sanchez M, Gibello A, Gutierrez F and Ferrer E. Propachlor Removal by Pseudomonas Strain GCH1 in an Immobilized-Cell System, Appl. Environ. Microbiol., vol. 66, pp.1190-1194, 2000.

[6] Tuzimski T and Rejczak T, Application of HPLC–DAD after SPE/QuEChERS with ZrO2-based sorbent in d-SPE clean-up step for pesticide analysis in edible oils, Food Chem., vol. 190, pp. 71–79, Jan. 2016.

[7] Qu JR, Zhang JJ, Gao YF and Yang H. Synthesis and utilisation of molecular imprinting polymer for clean-up of propachlor in food and environmental media, Food Chem., vol. 135, no. 3, pp. 1148–1156, Dec. 2012.

[8] Atılır Özcan A and Demirli Ş. Molecular Imprinted Solid-Phase Extraction System for the Selective Separation of Oleuropein from Olive Leaf, Sep. Sci. Technol., vol. 49, no. 1, pp. 74–80, 2014.

[9] Ambrosini S, Serra M, Shinde S, Sellergren B and Lorenzi E. De, Synthesis and chromatographic evaluation of molecularly imprinted polymers prepared by the substructure approach for the class-selective recognition of glucuronides, J. Chromatogr. A, vol. 1218, no. 39, pp. 6961–6969, 2011.

[10] K. Tang, X. Gu, Q. Luo, S. Chen, L. Wu, and J. Xiong, Preparation of molecularly imprinted polymer for use as SPE adsorbent for the simultaneous determination of five sulphonylurea herbicides by HPLC, Food Chem., vol. 150, pp. 106–112, 2014.

[11] Guo L, Deng Q, Fang G, Gao W and Wang S. Preparation and evaluation of molecularly imprinted ionic liquids polymer as sorbent for on-line solid-phase extraction of chlorsulfuron in environmental water samples, J. Chromatogr. A, vol. 1218, no. 37, pp. 6271–6277, 2011.

[12] Zarejousheghani M, Fiedler P, Möder M and Borsdorf H. Selective mixed-bed solid phase extraction of atrazine herbicide from environmental water samples using molecularly imprinted polymer, Talanta, vol. 129, pp. 132–138, 2014.

[13] Azizi A, Bottaro CS. A critical review of molecularly imprinted polymers for the analysis of organic pollutants in environmental water samples, J. Chromatogr. A, https://doi.org/10.1016/j.chroma.2019.460603, 2019.

[14] Q. He, J-J. Liang, L-X. Chen, S-L. Chen, H-L. Zheng, H-X. Liu and H-J. Zhang, Removal of the environmental pollutant carbamazepine using molecular imprinted adsorbents: Molecular simulation, adsorption properties, and mechanisms, Wat. Res., vol.168, pp.1-13,2020.

[15] Baydemir G, Bereli N, Andaç M, Say R, Galaev IY and Denizli A. Supermacroporous poly(hydroxyethyl methacrylate) based cryogel with embedded bilirubin imprinted particles, *React. Funct. Polym.*, vol. 69, no. 1, pp. 36–42, 2009.

[16] Ünlüer ÖB, Özcan A and Uzun L. Preparation of a novel hydrophobic affinity cryogel for adsorption of lipase and its utilization as a chromatographic adsorbent for fast protein liquid chromatography, Biotechnol. Prog., vol. 30, no. 2, pp. 376–382, 2014.

[17] Kanekiyo Y, Naganawa R and Tao H. pH-Responsive Molecularly Imprinted Polymers, Angew. Chem. Int. Ed., vol. 42, pp. 3014 – 3016, 2003.

[18] Akdamar HA, Yılmaz Sarıözlü N, Atılır Özcan A, Ersöz A, Denizli A, Say R. Separation and purification of hyaluronic acid by glucuronic acid imprintedmicrobeads, Mat. Sci. Engin. C, vol. 29, pp. 1404–1408, 2009.