



Nicotinamide-Modified poly(HEMA-GMA)-Nic Cryogels for Removal of Pesticides

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Abstract: Chlordane is only one of the persistent pesticides used in some countries despite the ban. Removal of chlordane, a severe threat to all living things, was performed using nicotinamide-modified poly(2-hydroxyethyl methacrylate-glycidyl methacrylate), poly(HEMA-GMA)-Nic, polymeric cryogels in this study. Poly(HEMA-GMA) polymeric cryogels were synthesized based on previously reported literature procedures and were subsequently modified by nicotinamide moieties. Removal of chlordane in alcoholic medium has been accomplished exploiting the alcho-phobic interaction, which was the first indication in our previous study. Structural analysis of poly(HEMA-GMA)-Nic was performed using Fourier transform infrared spectroscopy (FT-IR) and elemental analysis methods. Scanning electron microscopy (SEM) was used to understand the surface morphology of cryogels. Surface area and cavity volume calculations were determined by applying N₂ adsorption method and swelling test. The interaction time and maximum adsorption capacity were identified as 5 minutes and 64.61 mg chlordane/g cryogel for 300 mg/L chlordane concentration and 108.818 mg chlordane/g cryogel for 800 mg/L chlordane concentration during the adsorption experiments. Cyclohexane, toluene, chloroform, dichloromethane, acetone, and acetonitrile were used as solvents to observe the solvent effect on adsorption of chlordane onto the polymeric material. As expected, the removal of chlordane was performed with the highest adsorption performance in cyclohexane with the lowest dielectric constant.

Keywords: Chlordane, Pesticide, Alcho-phobic, Cryogel, Nicotinamide.

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INTRODUCTION

The technical chlordane, which is a mixture of approximately 150 different chemicals, mainly contains three chlordane compounds, cis-chlordane (CC), trans-chlordane (TC), and trans-nonachlor (1, 2). Chlordane was at the forefront of 12 prohibited pesticides in the UNER Stockholm Convention, which was signed on persistent organic pollutants in 2001 (3). As a broad-spectrum pesticide used against insects and pests in many vegetable and fruit cultures, chlordane, which has been used for many years in the United

States of America (after the 1940s) and Japan (1980s), is almost insoluble in water, like other pesticides (4-7). Chlordane, which is considered to be one of the most harmful members of pesticides, is profoundly harmful to health, and a severe endocrine disruptor (8-11). Results of exposure to low doses of chlordane may be the symptoms such as a headache, vomiting, loss of consciousness while exposure to high doses can result in death (12, 13). Also, it has been revealed that chlordane is linked to diabetes in the recent researches (14).

Monitoring, removal and degradation studies have been performed up to date to deal with the persistent organic pollutants resistant to degradation (7, 15-23). These methods have disadvantages such as the need for experienced users, harmful chemicals, long-term experimental procedure. Therefore, it is necessary to find new ways to be able to remove unwanted compounds in a short process efficiently.

Polymeric cryogels have been used extensively in many studies over the last 20 years and continue to be used due to the advantages such as easy synthesis, adequate performance, and low cost (24-27). In particular, the micro- and macroporous structure of cryogels overcome the disadvantages in conventional techniques. The primary downside of cryogels over micro- and nano-adsorbents is that they seem to have a low surface area, but they also eliminate many problems coming from these adsorbents such as agglomeration, low yield, and the need for high-performance devices such as centrifuges (28-32). Polymeric cryogels have interconnected flow-channels providing the diffusion of the target molecule to the cavities of the cryogels, therefore, this provides a healthy interaction between the ligands on the surface of cryogels and the target molecules residing on the cavities for a while (33).

We have applied the modification of a polymeric structure used in affinity techniques. Nicotinamide was added as a ligand to the poly (HEMA-GMA) polymeric structure, which was previously used in some studies (34). As an adsorbent, poly (HEMA-GMA) polymeric cryogels have been modified using nicotinamide. The modification of poly(HEMA-GMA) with nicotinamide is quite rare in the literature. Ethanol was used instead of water as a solvent. The main reason for using ethanol is that chlordane does not dissolve in water as mentioned before. Also, various organic solvents were also used to measure the chlordane adsorption performance of the synthesized polymeric material in different solutions.

MATERIALS AND METHODS

Materials

2-Hydroxyethyl methacrylate (HEMA), ethylene glycol di-methacrylate (EGDMA), glycidyl methacrylate (GMA), nicotinamide (Nic), ammonium persulfate (APS), sodium dodecyl sulfate (SDS) and N,N,N',N'-tetramethyl ethylenediamine (TEMED) and chlordane

(C₁₀H₆Cl₈, analytical standard, PN: 442449) were obtained from Sigma-Aldrich (St. Louis, MO, USA). All experiments were conducted using freshly prepared deionized (DI, (18 MΩ.cm)) water.

Synthesis and Characterization

The mixture of GMA (500 µL), HEMA (5000 µL) and distilled water (6500 µL) was prepared as the monomer phase. The dispersing phase was prepared using 1 g of sodium lauryl sulfate (SLS), 25.60 mL of distilled water, and 2.4 mL of EGDMA. The two phases were then mixed. They were kept in ice cubes for 10-15 minutes. 20 mg of APS and 100 µL of TEMED were added to start the polymerization. The polymerization mixture was poured in between two glass plates to have a polymeric plate. The polymeric mixture in between the glass plates was kept at -20 °C for 24 hours. At the end of this period, the glass plates were removed, and the polymeric plate was cut in the shape of a disk. The polymeric cryogel discs were washed with distilled water many times to remove unwanted chemicals. All cryogel disks were kept at +4 °C until use.

Some cryogel membranes (20 cryogel discs) were mixed with 1 M NaOH (10 mL) for 2 hours. Membranes washed several times with distilled water were incubated with 50 mg/mL nicotinamide solution (10 mL) for 24 hours. The aim of this process is to provide oxygen bonding of the epoxy groups of the GMA monomer of the amine groups in the nicotinamide molecules. Proof of Nic decoration can be observed by the color change from white to yellow.

For structural characterization of poly(HEMA-GMA)-Nic cryogels, Fourier transform infrared spectroscopy (FT-IR, Nicolet™ is™10 FTIR spectrometer, USA) and elemental analysis (CHNS-932, Leco, USA) methods were used. Surface morphology of the polymeric structure was observed in the course of the physical characterization. For this purpose, a scanning electron microscope (SEM, Carl Zeiss AG - EVO® 50 Series, Germany) was used. Also, surface area estimation of the cryogels was crucial for the successful interaction process. Surface area calculations were performed using the BET equations using the AUTOSORPI 6B (Quantachrome Instruments, USA) N₂-adsorption method. At last, swelling test, the water holding capacity of the polymeric material, was calculated using Equation 1 given below. The water holding capacity is informative about analyte diffusion.

$$\text{Water uptake \%} = \left[\frac{W_{\text{swollen}} - W_{\text{dry}}}{W_{\text{dry}}} \right] \quad (\text{Eq. 1})$$

W_{swollen} : weight in grams of water-retained
 W_{dry} : weight in grams of dry cryogels.

The polymeric material that will serve as solid support has been given functional properties by adding nicotinamide to the synthesized

poly(HEMA-GMA) polymeric structure. The target molecule contains six chlorine atoms and therefore acts as a Lewis base. The need for the adsorbent to be a suitable Lewis acid will be met by the nitrogen molecule around the nicotinamide and the unpaired electrons on the nitrogen atom.

Thus, a substantial electrostatic interaction will take place, and the removal will be successful, as the Lewis acid-base interaction and consequently the dipole-dipole electrostatic interaction between the positively charged amine groups and the polymer-dependent amino acids and chlorine atoms in the chlordane structure. If no nicotinamide were added, the electron cloud on the GMA would push the electron cloud around the chlordane, and there would be no interaction. The quantitative adsorption performance of

poly(HEMA-GMA)-Nic polymeric cryogels was measured using a UV-Visible spectrophotometer (OPTIZEN POP UV/Vis, Mecasys Co., Ltd., Korea).

Adsorption Studies

To determine the amount of adsorbed chlordane on the polymeric material spectroscopically, the wavelength at which chlordane has the highest absorbance was scanned. The highest absorbance of chlordane was observed at 216 cm^{-1} (Figure 1). This result is consistent with the literature (35).

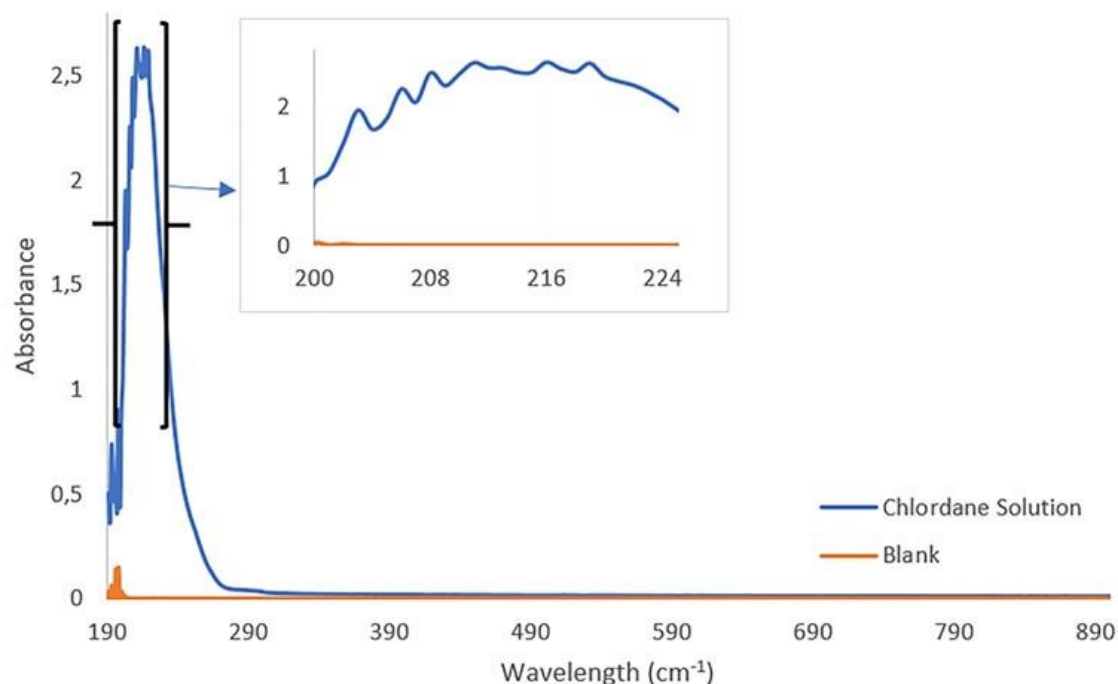


Figure 1. Maximum wavelength survey taken from the UV spectrum.

Adsorption experiments were carried out using 2 mL of chlordane (taken from 500 ppm stock solution)/8 mL of ethanol (98% v/v) in closed test tubes since the solvent is a volatile chemical. Chlordane (2 mL) was added to ethanol and homogenized for 15 minutes to ensure physical equilibrium. The disk-shaped cryogels, which were introduced to the adsorption solution, were then interacted with the chlordane during the optimum period determined by preliminary

experiments. The amount of chlordane adsorbed on the polymeric cryogels was calculated using Equation 2. Chloride solutions with concentrations ranging from 200-1000 mg/L were used to determine the chlordane saturation concentration capacities of the synthesized polymeric cryogels. All solutions were prepared using stock solutions of 500 and 1000 mg of chlordane/L ethanol.

$$q = \frac{[(C_i - C_f) \times V]}{m} \quad (\text{Eq. 2})$$

q : adsorption capacity in mg/g,

C_i : amount of chlordane before adsorption in mg/L

C_f : amount of chlordane after adsorption in mg/L

V : volume of the adsorption medium in mL

m : absorbance in g.

RESULTS and DISCUSSION

Characterization

The synthetic procedure of the poly (HEMA-GMA)-Nic polymeric cryogels used as adsorbents in this study is shown in Figure 2. As can be seen from the figure, the oxirane ring on the glycidyl methacrylate is opened when the nicotinamide is

attached. A bond was formed in between oxirane ring and amide end of nicotinamide. According to the FT-IR results, the peaks in the region of 1200-1700 cm^{-1} originating from the nitrogen atom on the nicotinamide are the most prominent indicators that nicotinamide is involved in the structure (Figure 3A). The characteristic poly (HEMA-GMA) peaks given by green circles are the peaks at 343.11 (-OH from HEMA), 1733.44 (-C=O from HEMA), 1247.75 and 903.35 cm^{-1} (36, 37). C-H, C = O, N-H, C = N, C-NH₂, C-N stretching and C-N-C bending peaks of the nicotinamide indicated by red circles were observed at 2931.48, 1680.46, 1571.55, 1274.24, 1160.56 and 520.69 cm^{-1} , respectively

(38). As a conclusion, 18.10^{-4} mole of nicotinamide has been successfully incorporated into the poly(HEMA-GMA) polymeric structure.

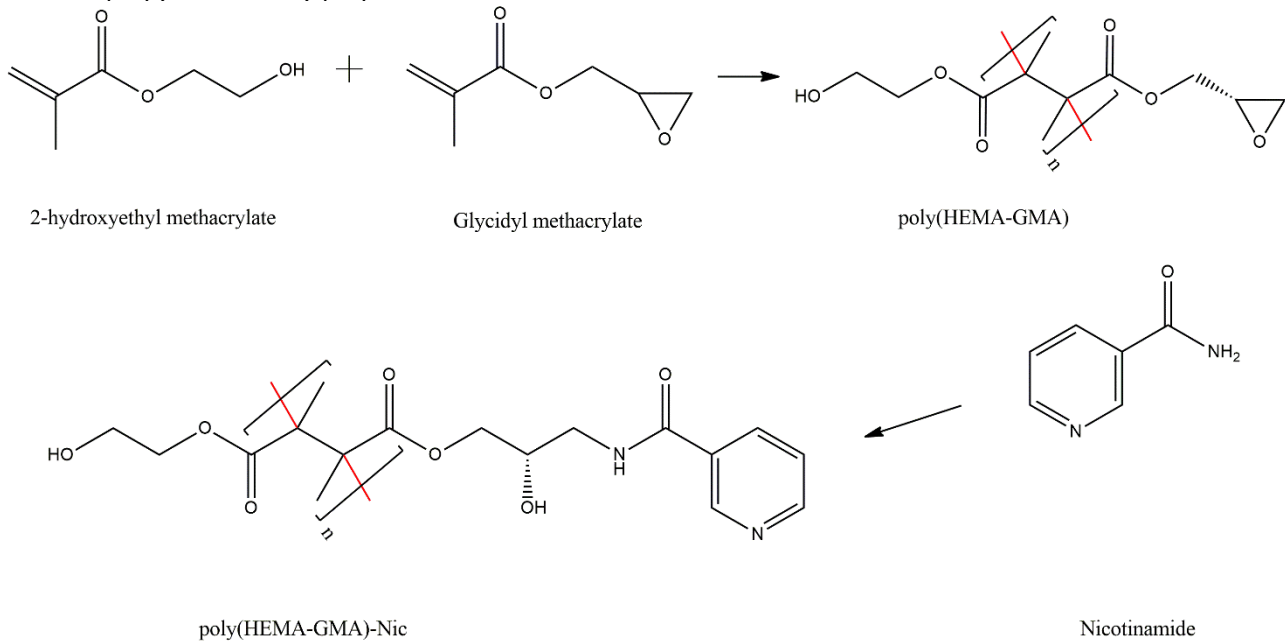


Figure 2. Schematic diagram of Poly(HEMA-GMA)-Nic polymeric cryogels.

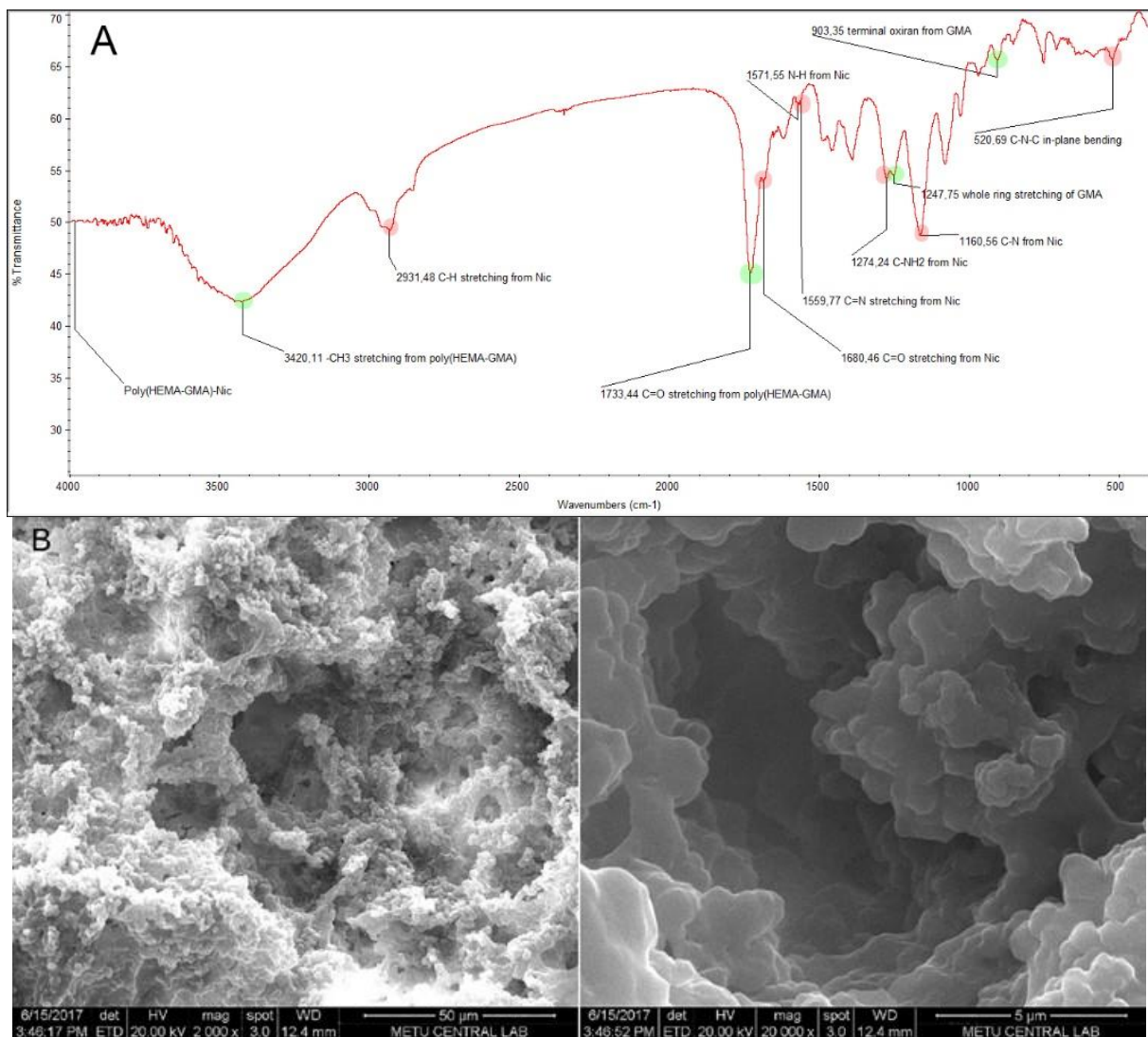


Figure 3. A) FT-IR spectrum and **B)** SEM images of poly(HEMA-GMA)-Nic polymeric cryogels

As can be seen from Figure 3B, the synthesized cryogels have cavities that allow the analyte to diffuse readily. The presence of holes in the porous structure, having a water retention capacity of about ~800%, although having a surface area of ~8.5 m²/g less than microparticles or nanoparticles (28-32, 39), provides the necessary retention time for the analyte to interact with ligand within polymeric structure. Ability to swallow high amount of analytes and the cavities connected with interconnected flow channels are the critical

properties of cryogels providing them to be indispensable absorbents.

To increase the strength of electrostatic attraction, the addition of iron cation with oxidation number 2 caused changes in the morphological structure of polymeric cryogels, such as the disappearance of the cavities and the appearance of needle-like structures (Figure 4). It is thought that the degradation of the surface morphology affects the adsorption kinetics in the negative direction.

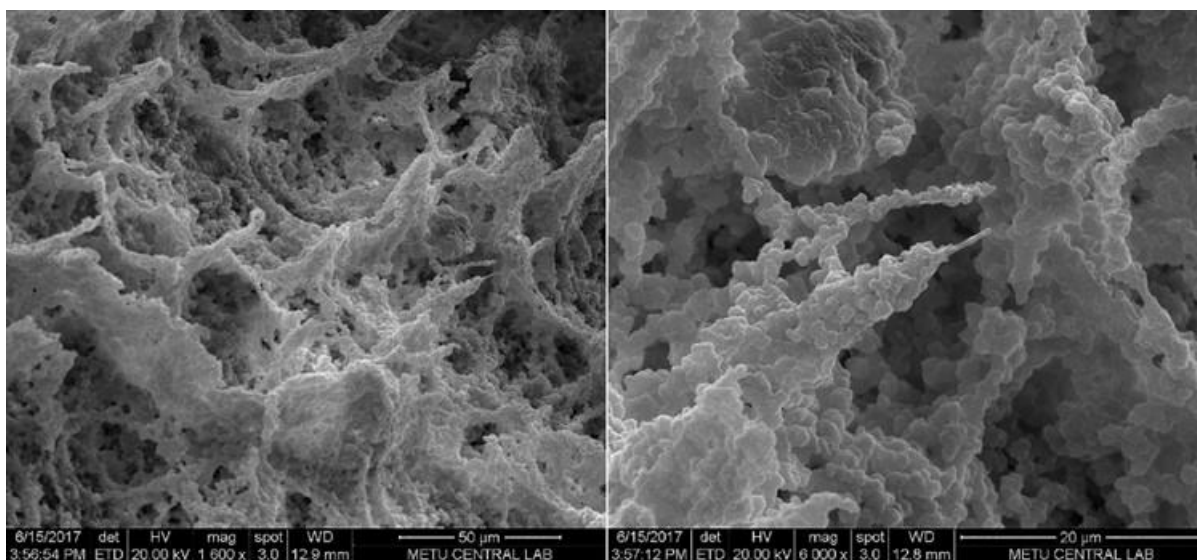


Figure 4. SEM images of Fe²⁺-decorated polymeric cryogels

Adsorption Studies

Since the chlordane is not soluble in water, all experiments were carried out in ethanol (98% v/v) (40). The eight chlorine atoms around the chlordane form a dense electron cloud around the molecule. Therefore, the adsorbent expected to interact with chlordane should have binding sites with positive charges. However, the structure of poly(HEMA-GMA) shows that the electron density is high in the periphery of GMA. To overcome this obstacle, decoration of nicotinamide to the polymeric structure will provide a positive charge, and thus it will act as a Lewis base. Nicotinamide is attached to the polymeric material from the -NH₂ end (Figure 2). Due to the resonance stability of the pyridine ring, the N atom within the ring is partially positively charged. Also, the unpaired electron on the nitrogen atom of the pyridine ring will also contribute to the electrostatic interaction by allowing the molecule to behave like a Lewis base. Fe²⁺ ions were added to the structure to increase the electrostatic attraction force of the structure. However, low adsorption was observed on the contrary to expectation (41). In their work, Köse and Köse, added Ni²⁺, Cu²⁺ and Co²⁺ ions to the structure to increase electrostatic force, but they have observed a decrease in the adsorption of the pesticides to the polymeric adsorbent (42). As a result, poly(HEMA-GMA)-Nic without Fe²⁺ was used in all experiments. The electron cloud around the chlordane molecule causes electrostatic attraction because of the existence

of eight chlorine atoms to create the desired interaction with the Nic molecule linked to the ligand of the polymeric material. The pK_a value of the nicotinamide molecule is 3.35 (43). Thus the partially positively charged N atom and the stable pyridine ring because of resonance phenomenon meet this requirement in the adsorption environment with neutral pH value. However, the carbonyl structure found in the nicotinamide molecule repels the -OH moieties and thus the partially positively charged N-atom in the pyridine ring does the -CH₂-CH₃ moieties of the ethanol molecules. In the same way, chlordane will cause ethanol to move away due to its massive structure, dense electron cloud, and its 3-dimensional structure. The ethanol will be withdrawn from between interacting groups, the alcohol-phobic interaction, resulting in a substantial electrostatic interaction between chlordane and poly(HEMA-GMA)@Nic polymeric cryogels (40) (Figure 5A). The adsorption of chlordane on the surface of cryogels can be seen clearly in Figure 5B, the surface morphology of poly(HEMA-GMA)-Nic cryogels was changed. In the meantime, decorating the Nic molecules causes an increase in the route of the electrons traveling on around of the Nic molecule itself. Therefore, the time for the presence of the partially positive charge clouds on the Nic was increased. Thus, the interaction between Nic and the chlordane will be stronger. It is significantly important that because the ethanol does not have

ionization ability, it meets the requirement as a solvent for an ideal electrostatic interaction.

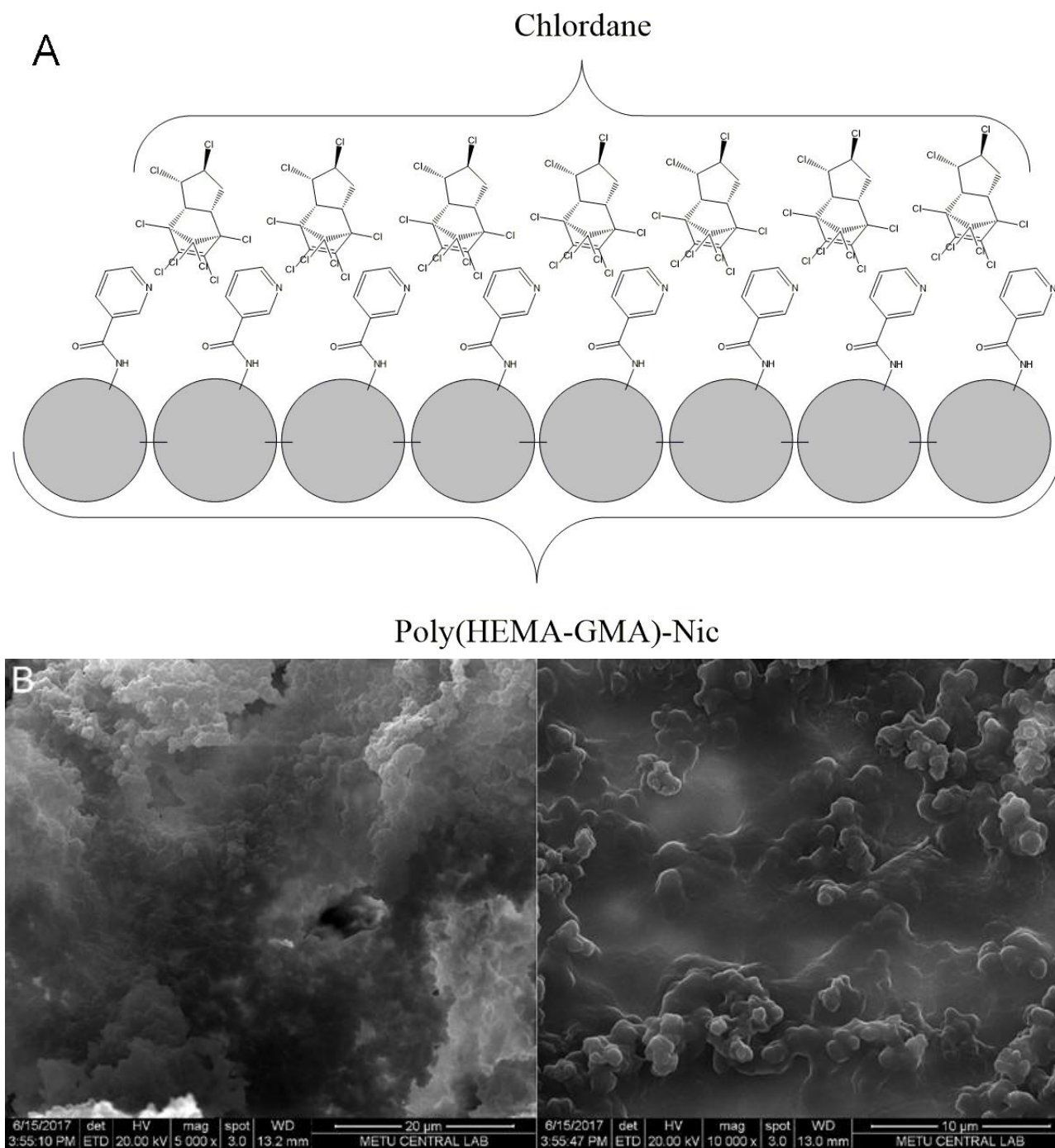


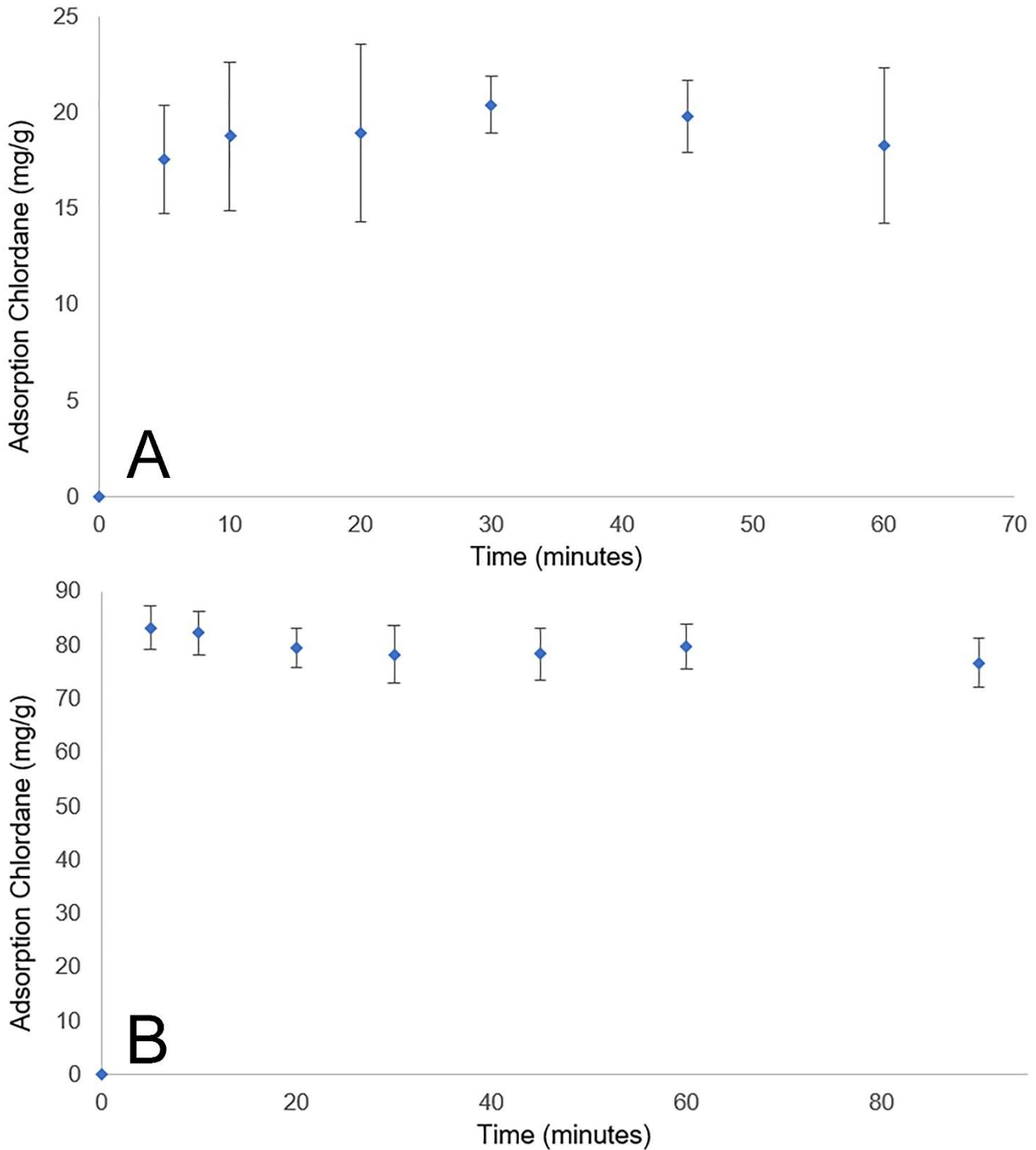
Figure 5. A) Expected interaction between poly(HEMA-GMA)-Nic cryogels and chlordane molecules, B) Chlordane adsorbed poly(HEMA-GMA)-Nic cryogels.

As can be seen from Figure 6, the chlordane adsorption performance of poly(HEMA-GMA)-Nic cryogels was investigated at varying time intervals for different chlordane concentrations. Moreover, the effect of initial chlordane concentration on the adsorption performance of the polymeric material was determined. All experiments were repeated three times, and standard deviations were calculated. Adsorption experiments were carried out at concentrations of 100, 200 and 300 mg chlordane/ethanol to determine the effect of concentration on the optimum adsorption time. As expected, the

increased concentration of chlordane increased the amount of adsorption but no significant change in the time of interaction was observed. The interaction was completed within the first 5 minutes (Figure 6a-b-c). A plateau was observed in all plots after five minutes, which is attributed to the fact that all binding sites of the polymeric cryogels were saturated by the chlordane. Likewise, Figure 6d shows how the increased chlordane initial concentration affects the adsorption performance of polymeric cryogels. As can be seen, adsorption process increased up to 800 mg chlordane/L ethanol concentration, after

which a plateau was observed in the graph. This value is critical regarding the adsorption amount of 108.818 mg of chlordane/L ethanol for a short period of 5 minutes for each same-sized cryogel disk. This value achieved by the removal of chlordane is quite comparable to similar studies in the literature (17, 44, 45). At the same time,

as mentioned above, all of the binding sites of a cryogel disk were engaged with the target molecules, chlordane. It can be concluded that the poly(HEMA-GMA)-Nic cryogels can be a good candidate for every concentration of pesticides, i.e., very low and very high amount of pesticide.



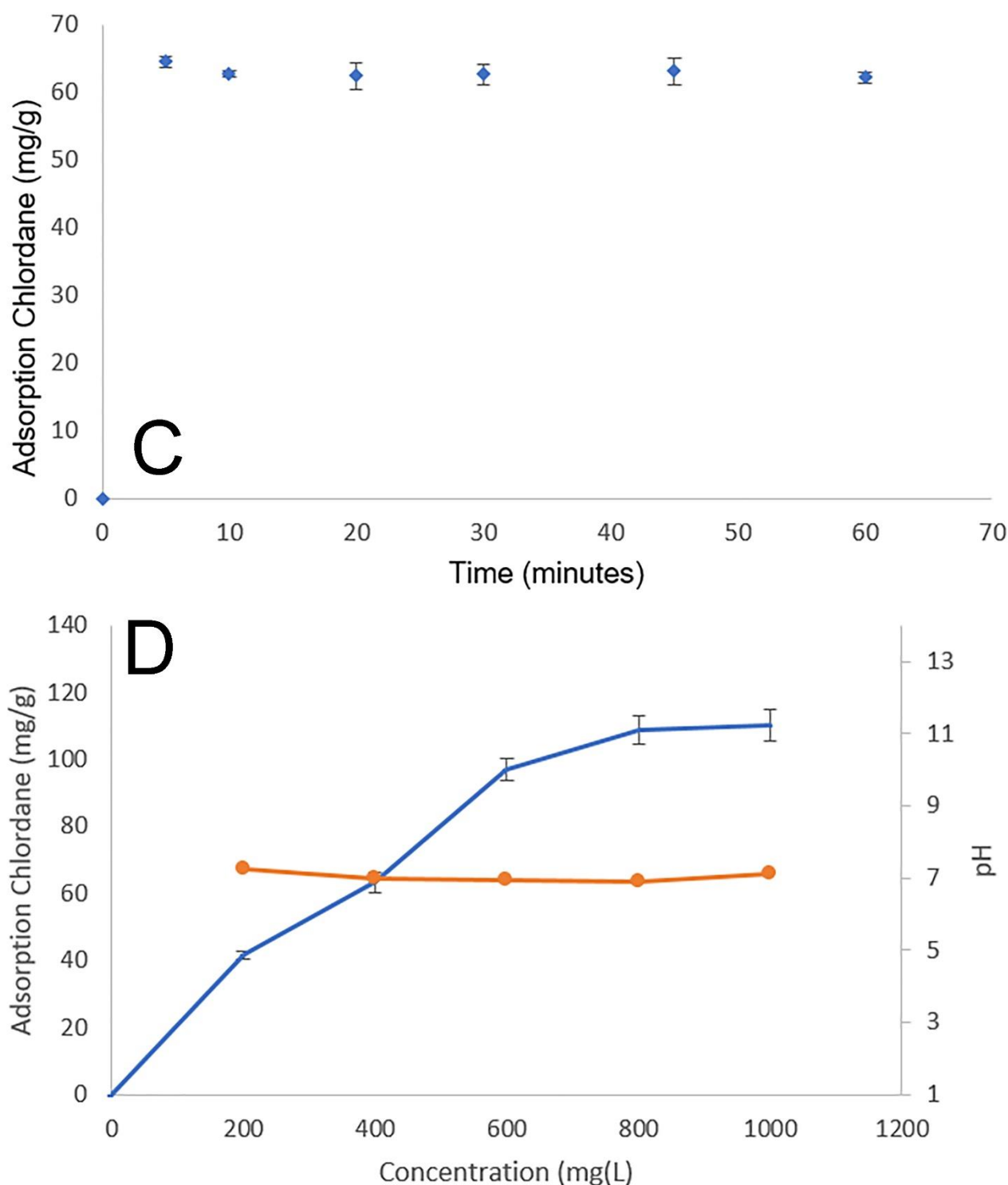


Figure 6. Parameters for chlordane adsorption process: A) $t_{\text{interaction}}$; $C_{\text{chlordane}}$: 100 mg/L, pH: 7.0 (ethanol medium), T: 25°C, B) $t_{\text{interaction}}$; $C_{\text{chlordane}}$: 200 mg/L, pH: 7.0 (ethanol medium), T: 25°C, C) $t_{\text{interaction}}$; $C_{\text{chlordane}}$: 300 mg/L, pH: 7.0 (ethanol medium), T: 25°C, D) $C_{i,\text{chlordane}}$; pH: 7.0 (ethanol medium), $t_{\text{Adsorption}}$: 10 min, T: 25°C.

Like other pesticides, chlordane is highly soluble in organic solvents (46, 47). The adsorption performances in the solutions containing chlordane molecules and solvents such as cyclohexane, toluene, chloroform, dichloromethane, acetone and acetonitrile solvents were compared with that in ethanol to observe how the chemical structures of the solvents affected the interaction between the

polymeric cryogels and the chlordane in this study (Figure 7). Since the dielectric coefficients of organic solvents mentioned are different (48), the solubility of chlordane and therefore the electrostatic interaction in between will be different. At the end of the adsorption experiments, a correlation was observed between the dielectric coefficients and the adsorption performance. The solvent with a relatively high

dielectric constant will separate the opposing charges better which is the primary requirement for stronger electrostatic interaction. Therefore, electron cloud formation will occur smoothly and so thus proton clustering (49). As seen in Figure 7, the solubility of the chlordane in cyclohexane and hence its adsorption on the polymeric material is the highest. All works were performed in ethanol although the performances in other organic solvents were higher than that in ethanol.

The most important reasons for this are the toxicity (50) and cost of these organic solvents. Moreover, polymeric materials have been gone deformation during adsorption in acetone and acetonitrile. Therefore, it is more feasible to use the least harmful chemical in the adsorption process. Also, studies performed in ethanol have been carried out, and very positive results have been obtained in the literature (40).

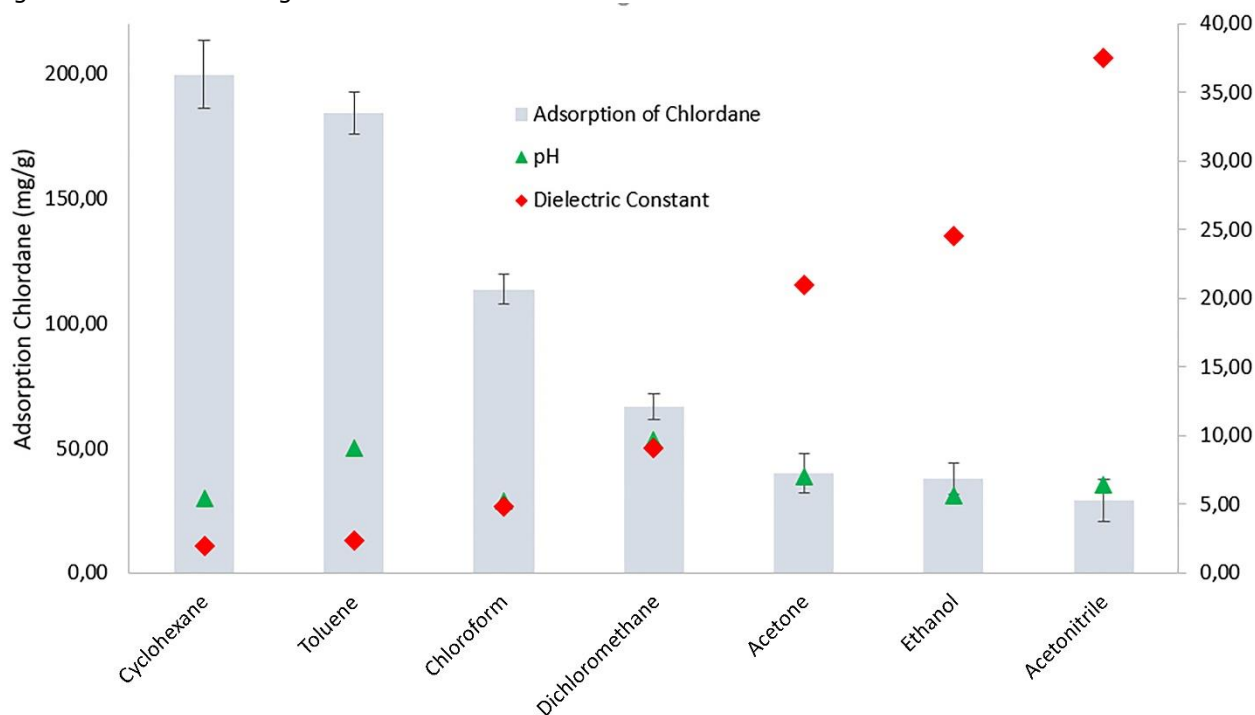


Figure 7. Solvent effect on the chlordane adsorption.

Mathematical calculations performed to characterize the interaction between the polymeric material and chlordane indicate that the adsorption is chemically controlled and homogeneous. The chemical character of the interaction is determined by pseudo-first and -second-order kinetic models and results are given in Table 1. As can be seen, the correlation coefficient (R^2) obtained with the pseudo-second-order kinetic model is very close to unity. Moreover, the theoretically calculated adsorption amount of chlordane is almost similar to that obtained experimentally. The polymeric cryogels acted virtually like a chemical adhesive throughout the adsorption.

The degree of homogeneity and non-specific interactions are determined by Langmuir and Freundlich adsorption isotherm calculations. According to the values given in Table 2, the correlation constant obtained for the Langmuir adsorption model is closer to 1 than the value obtained in the Freundlich model calculations. Furthermore, the fact that the b value is close to 0 and the experimental and theoretical Q values are nearly the same indicates that the interaction in this study is more appropriate for the Langmuir adsorption model. The interaction was homogeneous in a single layer and resulted in no interaction between neighboring regions.

Table 1. Chemical kinetic parameters for the chlordane-poly(HEMA-GMA)-Nic interaction.

Chemical Kin.		Pseudo-First Order			Pseudo-Second Order		
In. Conc. (mg/L)	Q _{exp.} (mg/g)	Q _{calc.} (mg/g)	k ₁ (1/min.)	R ²	Q _{calc.} (mg/g)	k ₂ (g/mg.min)	R ²
100	20.41	2.89	-0.35	0.9467	20.33	0.06	0.9986
200	46.82	0.71	0.04	0.6670	43.48	0.05	0.9999
300	64.61	1.45	0.00	0.0570	62.89	0.63	0.9999

Table 2. Adsorption isotherm parameters for the chlordane-poly(HEMA-GMA)-Nic interaction.

Adsorption Isotherms	Langmuir Adsorption Isotherm				Freundlich Adsorption Isotherm		
Equations	$\frac{1}{Q_{eq}} = \left[\frac{1}{Q_{max} \cdot b} \right] \left[\frac{1}{C_{eq}} \right] + \left[\frac{1}{Q_{max}} \right]$				$\ln Q_{eq} = \ln K_F + \frac{1}{n} \ln C_{eq}$		
Linear Equation	$y = 1.1208x + 0.0066$				$y = 0.4961x + 1.7118$		
Cryogel / Parameters	Q _{exp}	Q _{max} (mg/g)	b (L/mg)	R ²	K _F	1/n	R ²
Poly(HEMA-GMA)-Nic	110.19	151,51	0,0058	0.9946	5,5389	2,0157	0.9714

CONCLUSION

In this study, the previously synthesized poly(HEMA-GMA) polymeric material was modified with Nic, and chlordane removal performance in ethanol was investigated. As a first step of the study, poly(HEMA-GMA) polymeric material was synthesized and modified with nicotinamide monomer.

Successful Nic-decoration on the poly(HEMA-GMA) cryogels was confirmed with the presence of bending and stretching of N containing bonds in the FT-IR plot. The porous and 3-dimensional structure of polymeric cryogel were approved SEM images. Changes in the surface morphology given by SEM images also is also a proof of chlordane adsorption. Chlordane molecules were adsorbed on the poly(HEMA-GMA)-Nic quite fast. The highest chlordane adsorption capacity was achieved at the chlordane concentration of 800 mg/L as 108.818 mg/g. According to the experimental results, Nic-decoration enhances the Lewis acid-base interaction between polarized chlordane shell and poly(HEMA-GMA) polymeric solid support. This polarization causes the inductive polarization of Nic decorated on the polymeric material. As mentioned in the text, Nic decoration increases the pathway of an electron on the Nic along the whole polymeric structure, so thus the time of being positively charged. As a conclusion, poly(HEMA-GMA)-Nic cryogels can be used efficiently for the removal of pesticides from alcohol matrix. Therefore, it is the main advantages of this method over the traditional removal methods with some difficulties. It is claimed by this study that formation of alcohol-phobic interaction enables adsorption of chlordane in ethanol.

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REFERENCES

- Xiao P, Mori T, Kondo R. Biotransformation of the organochlorine pesticide trans-chlordane by wood-rot fungi. *New biotechnology*. 2011;29(1):107-15.
- Dearth MA, Hites RA. Highly chlorinated dimethanofluorenes in technical chlordane and in human adipose tissue. *Journal of the American Society for Mass Spectrometry*. 1990;1(1):99-103.
- Hirano T, Ishida T, Oh K, Sudo R. Biodegradation of chlordane and hexachlorobenzenes in river sediment. *Chemosphere*. 2007;67(3):428-34.
- Eitzer BD, Mattina MI, Iannucci-Berger W. Compositional and chiral profiles of weathered chlordane residues in soil. *Environmental toxicology and chemistry*. 2001;20(10):2198-204.
- Ouyang Y, Ou L-T, Sigua G. Characterization of the pesticide chlordane in estuarine river sediments. *Journal of environmental quality*. 2005;34(2):544-51.
- Taguchi S, Yakushiji T. Influence of termite treatment in the home on the chlordane concentration in human milk. *Arch Environ Con Tox*. 1988;17(1):65-71.

7. Janouskova E, Krbuskova M, Rehurkova I, Klimova M, Prokes L, Ruprich J. Determination of chlordane in foods by gas chromatography. *Food chemistry*. 2005;93(1):161-9.
8. Council NR. An assessment of the health risks of seven pesticides used for termite control. 1982.
9. Combarrous Y. Endocrine Disruptor Compounds (EDCs) and agriculture: The case of pesticides. *Comptes Rendus Biologies*. 2017;340(9):406-9.
10. Yadav IC, Devi NL, Li J, Zhang G, Breivik K. Possible emissions of POPs in plain and hilly areas of Nepal: implications for source apportionment and health risk assessment. *Environmental pollution*. 2017;220:1289-300.
11. Goldner WS, Sandler DP, Yu F, Hoppin JA, Kamel F, LeVan TD. Pesticide use and thyroid disease among women in the Agricultural Health Study. *American journal of epidemiology*. 2010;171(4):455-64.
12. Shindell S, Ulrich S. Mortality of workers employed in the manufacture of chlordane: an update. *Journal of occupational medicine: official publication of the Industrial Medical Association*. 1986;28(7):497-501.
13. MacMahon B, Monson RR, Wang HH, Zheng T. A second follow-up of mortality in a cohort of pesticide applicators. *Journal of occupational medicine: official publication of the Industrial Medical Association*. 1988;30(5):429-32.
14. Everett CJ, Matheson EM. Biomarkers of pesticide exposure and diabetes in the 1999–2004 National Health and Nutrition Examination Survey. *Environment international*. 2010;36(4):398-401.
15. Wu X, Lam JC, Xia C, Kang H, Xie Z, Lam PK. Atmospheric concentrations of DDTs and chlordanes measured from Shanghai, China to the Arctic Ocean during the Third China Arctic Research Expedition in 2008. *Atmospheric environment*. 2011;45(22):3750-7.
16. Vorkamp K, Møller S, Falk K, Rigét FF, Thomsen M, Sørensen PB. Levels and trends of toxaphene and chlordane-related pesticides in peregrine falcon eggs from South Greenland. *Science of the Total Environment*. 2014;468:614-21.
17. Fuentes MS, Raimondo EE, Amoroso MJ, Benimeli CS. Removal of a mixture of pesticides by a *Streptomyces* consortium: Influence of different soil systems. *Chemosphere*. 2017;173:359-67.
18. Man YB, Chow KL, Cheng Z, Kang Y, Wong MH. Profiles and removal efficiency of organochlorine pesticides with emphasis on DDTs and HCHs by two different sewage treatment works. *Environmental Technology & Innovation*. 2017.
19. Kida M, Ziembowicz S, Koszelnik P. Removal of organochlorine pesticides (OCPs) from aqueous solutions using hydrogen peroxide, ultrasonic waves, and a hybrid process. *Separation and Purification Technology*. 2018;192:457-64.
20. Kim S, Chu KH, Al-Hamadani YA, Park CM, Jang M, Kim D-H, et al. Removal of contaminants of emerging concern by membranes in water and wastewater: A review. *Chemical Engineering Journal*. 2017.
21. Yamada S, Naito Y, Funakawa M, Nakai S, Hosomi M. Photodegradation fates of cis-chlordane, trans-chlordane, and heptachlor in ethanol. *Chemosphere*. 2008;70(9):1669-75.
22. Cuozzo SA, Fuentes MS, Bourguignon N, Benimeli CS, Amoroso MJ. Chlordane biodegradation under aerobic conditions by indigenous *Streptomyces* strains. *Int Biodeter Biodegr*. 2012;66(1):19-24.
23. Fang Y, Nie Z, Die Q, Tian Y, Liu F, He J, et al. Organochlorine pesticides in soil, air, and vegetation at and around a contaminated site in southwestern China: Concentration, transmission, and risk evaluation. *Chemosphere*. 2017;178:340-9.
24. Gun'ko VM, Savina IN, Mikhalovsky SV. Cryogels: Morphological, structural and adsorption characterisation. *Advances in Colloid and Interface Science*. 2013;187-188:1-46.
25. Erol K. The Adsorption of Calmoduline via Nicotinamide Immobilized Poly (HEMA-GMA) Cryogels. *Journal of the Turkish Chemical Society, Section A: Chemistry*. 2017;4(1):133-48.
26. Erol K. Polychelated cryogels: hemoglobin adsorption from human blood. *Artificial cells, nanomedicine, and biotechnology*. 2017;45(1):31-8.
27. Erol K, Uzun L. Two-step polymerization approach for synthesis of macroporous surface ion-imprinted cryogels. *Journal of Macromolecular Science, Part A*. 2017;54(11):867-75.
28. Kose K, Denizli A. Poly(hydroxyethyl methacrylate) based magnetic nanoparticles for lysozyme purification from chicken egg white. *Artif Cells Nanomed Biotechnol*. 2013;41(1):13-20.

29. Yilmaz F, Kose K, Sari MM, Demirel G, Uzun L, Denizli A. Bioinspired surface modification of poly(2-hydroxyethyl methacrylate) based microbeads via oxidative polymerization of dopamine. *Colloid Surface B*. 2013;109:176-82.
30. Kose K, Erol K, Emniyet AA, Kose DA, Avci GA, Uzun L. Fe(II)-Co(II) Double Salt Incorporated Magnetic Hydrophobic Microparticles for Invertase Adsorption. *Appl Biochem Biotechnol*. 2015;177(5):1025-39.
31. Kose K. Nucleotide incorporated magnetic microparticles for isolation of DNA. *Process Biochem*. 2016;51(10):1644-9.
32. Kose K. Characterization of Magnetic Polymeric Microparticles. *Journal of the Turkish Chemical Society, Section A: Chemistry*. 2016;3(3):185-204.
33. Lozinsky VI, Galaev IY, Plieva FM, Savina IN, Jungvid H, Mattiasson B. Polymeric cryogels as promising materials of biotechnological interest. *Trends Biotechnol*. 2003;21(10):445-51.
34. Bayramoğlu G, Yalçın E, Arica MY. Characterization of polyethylenimine grafted and Cibacron Blue F3GA immobilized poly (hydroxyethylmethacrylate-co-glycidylmethacrylate) membranes and application to bilirubin removal from human serum. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2005;264(1-3):195-202.
35. Gore RC, Hannah RW, Pattacini SC, Porro TJ. Infrared and ultraviolet spectra of seventy-six pesticides. *Journal of the Association of Official Analytical Chemists*. 1971;54(5):1040-82.
36. Doğan A, Özkara S, Sarı MM, Uzun L, Denizli A. Evaluation of human interferon adsorption performance of Cibacron Blue F3GA attached cryogels and interferon purification by using FPLC system. *J Chromatogr B*. 2012;893-894(Supplement C):69-76.
37. Akduman B, Uygun M, Uygun DA, Akgöl S, Denizli A. Purification of yeast alcohol dehydrogenase by using immobilized metal affinity cryogels. *Materials Science and Engineering: C*. 2013;33(8):4842-8.
38. Ramalingam S, Periandy S, Govindarajan M, Mohan S. FT-IR and FT-Raman vibrational spectra and molecular structure investigation of nicotinamide: A combined experimental and theoretical study. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2010;75(5):1552-8.
39. Erol K, Kose K, Kose DA, Sizer U, Satir IT, Uzun L. Adsorption of Victoria Blue R (VBR) dye on magnetic microparticles containing Fe(II)-Co(II) double salt. *Desalin Water Treat*. 2016;57(20):9307-17.
40. Köse K, Köse DA. Removal of DDE by exploiting the alcohol-phobic interactions. *Environmental Science and Pollution Research*. 2017;24(10):9187-93.
41. Lalah JO, Njogu S, Wandiga S. The effects of Mn²⁺, Ni²⁺, Cu²⁺, Co²⁺ and Zn²⁺ ions on pesticide adsorption and mobility in a tropical soil. *Bulletin of environmental contamination and toxicology*. 2009;83(3):352-8.
42. Kose K, Kose DA. Removal of DDE by exploiting the alcohol-phobic interactions. *Environ Sci Pollut Res Int*. 2017;24(10):9187-93.
43. Perrin DD. Ionisation constants of inorganic acids and bases in aqueous solution: Elsevier; 2016.
44. Dobbs RA, Cohen JM. Carbon adsorption isotherms for toxic organics: Municipal Environmental Research Laboratory, Office of Research and Development, US Environmental Protection Agency; 1980.
45. Murray R, Phillips P, Bender J. Degradation of pesticides applied to banana farm soil: comparison of indigenous bacteria and a microbial mat. *Environmental toxicology and chemistry*. 1997;16(1):84-90.
46. Tomlin C. The e-Pesticide manual: a world compendium, 11th edn., Version 1.1, Farnham. British Crop Protection Council. 1999.
47. Worthing CR, Walker SB, Flores G, Hilje L, Mora G, Carballo M. The Pesticide Manual, A World Compendium. The British Crop Protection Council. Londres (RU). 1987.
48. Maryott AA, Smith ER. Table of dielectric constants of pure liquids. National Bureau of Standards Gaithersburg MD; 1951.
49. Paruta AN, Sciarrone BJ, Lordi NG. Correlation between solubility parameters and dielectric constants. *Journal of pharmaceutical sciences*. 1962;51(7):704-5.
50. Lvet A, Bordes C, Clément Y, Mignon P, Chermette H, Marote P, et al. Quantitative structure-activity relationship to predict acute fish toxicity of organic solvents. *Chemosphere*. 2013;93(6):1094-103.