SYNTHESIS OF MOLECULARLY IMPRINTED POLYMER OF BISPHENOL A GLYCEROLATE DIMETHACRYLATE (BIS-GMA/FA) FOR FORMALDEHYDE RECOGNITION SYSTEM IN AQUEOUS MEDIUM

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Abstract. Imprinted Polymer of Bisphenol A Glycerolate Dimethacrylate/formaldehyde (Bis-GMA/FA) was synthesized using bisphenol A glycerolate dimethacrylate (Bis-GMA) (functional monomer), triethylene glycol-dimethacrylate (TEGDMA) (cross linker) and formaldehyde (FA) as a template molecule via photopolymerization (380 – 515 nm) for 60 seconds. Elimination of template from polymer was done with methanol/acetic acid (9/1) for 8 hours. The FTIR spectrum showed that the broad peak at 1650 – 1750 cm^{-1} region in Bis-GMA/FA become sharp after washing demonstrating the elimination of excessive carbonyl group (formaldehyde). The surface morphology of Bis-GMA/FA showed the presence of pores as compared to non-imprinted polymer of Bisphenol A Glycerolate Dimethacrylate (Bis-GMANIP). The recognition study demonstrated that Bis-GMA/FA with 0.1% template exhibit higher binding capacity (0.19 mgg^{-1}) for formaldehyde as compared to other Bis-GMA/FA and Bis-GMANIP. Freundlich isotherm showed good heterogeneity (n = 0.702) of Bis-GMA/FA and formaldehyde in an aqueous medium.

Keywords: Molecularly imprinted polymer, formaldehyde, molecular recognition, rebinding, isotherm

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Introduction

Formaldehyde is a volatile and dangerous organic compound, a highly toxic pollutant, and one of the most common indoor gas pollutants used in various industries, including manufacturing, food processing, and others. Even at very low concentrations, formaldehyde poses significant risks to humans, as evidenced by the direct effect of formaldehyde on the carcinogenicity of the organism's cells and inhalation of formaldehyde is a cause of human mucous membrane rupture [1]. Untreated and partially treated wastewater from industries such as pharmaceuticals, pulp and paper, resins and adhesives, and textiles contains organic and inorganic compounds such as phenolic compounds, dye, formaldehyde, and heavy metals, all of which are major water polluters.The discharge of untreated effluent from industries will cause a major problem in the water stream. Therefore, various methods have been employed to remove hazardous materials from the water stream. Adsorptions are the most effective method [2].

Adsorptions are well known for their efficiency and simplicity that uses different types of absorbents for removing the target or analyte molecules from aqueous medium systems [3]. The most commonly used adsorbent is activated carbon, which can be prepared from a variety of sources such as plants and wood and then treated to achieve the best properties such as excellent adsorption capacity and effective surface area [4]. Furthermore, due to the recognition system assessment, molecularly imprinted polymer (MIP) has become an attraction in the adsorption or removal of various types of target molecules in the aqueous medium, providing fast and high extraction efficiency, high adsorption capacity, and fast mass transfer [5]. MIP synthesis can be carried out in several types of polymerizations, such as bulk, photo-polymerization, and suspension. The polymerization process is carried out in the presence of the initiator, monomer, cross-linker and template molecules. The templates are used to create recognition sites in polymers that are in turn used to design functional monomers to synthesize the effective MIPs made in the imprinting process. MIPs exhibit high selectivity and affinity during polymerization. In the molecular imprinting process of synthetic polymers, monomers and cross-linkers are copolymerized with the template molecules, which MIPs were able to re-bind the templates in the aqueous medium under the optimum conditions of adsorption parameters in the various fields of chemical analysis [6]. After polymerization, templates are removed from MIPs, leaving cavities with specific binding sites [7]. In this study, formaldehyde imprinted molecular polymers were synthesized in an aqueous medium using photo irradiation with Bisphenol A glycerolate dimethacrylate (Bis-GMA), triethylene glycol-dimethacrylate (TEGDMA), 2,4-Dinitrophenylhydrazine (DNPH), and polyvinyl alcohol (PVA).

Materials and Methods

Bisphenol A glycerolate dimethacrylate (Bis-GMA, 99 % purity), triethylene glycol-dimethacrylate (TEGDMA, 95 % purity), and polyvinyl alcohol (PVA, 99 % purity), chemical compounds of Camphorquinone (CQ, 97 % purity) used as a photoinitiator and Ethyl 4-(dimethylamine)benzoate (EDMAB, 99 % purity) used as an accelerator of reaction were purchased from Sigma Aldrich. Formaldehyde was obtained from Merch KGaA (Darmstadt, Germany) on form formalin solution (37% formaldehyde). Acetyl acetone (99 % purity), acetic acid, ammonium acetate (99 % purity), dipotassium hydrogen phosphate (99 % purity) and potassium dihydrogen phosphate (99 % purity) for Fluoral-P preparation were

purchased from Systerm. Fluoral-P reagent, 97 % purity (2-amino-3-pentene-2-one was purchased from Aldrich.

Synthesis and Characterization of Bis-GMA/FA

Bisphenol A glycerolate dimethacrylate (Bis-GMA) (monomer) and triethylene glycol dimethacrylate (TEGDMA) (cross-linker) were mixed with 1 mL of 500 mgL^{-1} formaldehyde (37 wt%). The solution was homogeneous after one hour of stirring. The monomer/cross-linker ratio was varied in the ranges of 1:1, 1:2, and 2:1. Camphorquinone (CQ) (photoinitiator) and ethyl 4-(dimethylamine) benzoate (EDMAB) (accelerator) in acetonitrile (0.05 gmL^{-1}) were added to the mixture and stirred overnight. Polyvinyl alcohol (PVA) (2.5 g) was added to the mixture for the filler purpose and stirred for another 3 hours to achieve a homogeneous paste. The paste was placed in a teflon mold (10 mm in diameter and 1.5 mm in thickness) and cured with ultraviolet light (wavelength range 380 – 515 nm) for 60 seconds by photopolymerization technique. The polymerized paste (pellet) underwent the washing stage for 8 hours with a mixture of methanol/acetic acid (9/1 by v/v) in order to eliminate the template (formaldehyde). The pellet was kept dry in a sealed sample bottle after drying in an oven at 40 °C for further experiment. Characterization of Bis-GMA/FA was done using Perkin Elmer 100 Fourier Transform Infra-Red Spectroscopy to determine the functional group before and after washing stage Bis-GMA/FA. The Surface morphology of Bis-GMA/FA was examined by Field Emission Scanning Electron Microscope (FESEM) Hitachi 8U 8020 UHR.

Recognition Study of Formaldehyde in Aqueous Solution onto Bis-GMA/FA

The adsorption of formaldehyde onto Bis-GMA/FA was done for the recognition study of formaldehyde in an aqueous solution. The recognition or adsorption of formaldehyde onto Bis-GMA/FA included the optimum Bis-GMA/FA, kinetic and isotherm. The study of optimum Bis-GMA/FA at three different ratio was done by immersing its in 10 mL of formaldehyde solution for 10 minutes separately. After 10 minutes, the Bis-GMA/FA solutions were taken out, and 3 mL of the remaining solution was mixed with 4 mL of Fluoral-P reagent and 3 mL of phosphate buffer (pH 7). After 40 minutes of reaction, the absorbance intensity of the mixture was measured at 412 nm. The absorbance intensity of the same mixture without Bis-GMA/FA was also measured. The optimum experiment was continued with Bis-GMA/FA with different percentages of template (0, 0.01, 0.1, 0.2, 0.3, 0.4 and 0.5%). The experiment followed the same procedure as the optimum monomer ratio. The Fluoral-P reagent was prepared by adding 0.2 mL of acetyl acetone to 0.3 mL of acetic acid, dissolving 15.4 g of ammonium acetate into the solution and then completing the solution volume to 100 mL with deionized water [8]. About 3 mL of formaldehyde (20 mgL^{-1}) and 4 mL of Fluoral-P reagent were added with 3 mL of phosphate buffer pH 7. The solution was swirled to make it more homogenous. The absorbance intensity of the mixture was measured at 412 nm with an Agilent ultraviolet spectrophotometer after 40 minutes.

In the kinetic study, Bis-GMA/FA was immersed in 20 mL of 20 mgL^{-1} formaldehyde solution with different pH separately. The pH was varied (pH 2–10) by adding 0.1 M HCl and 0.1 M NaOH. The Bis-GMA/FA were also immersed in three different formaldehyde concentrations (5, 10, and 20 mgL^{-1}) at various time intervals for 48 hours (0, 0.5, 1, 2, 3, 4, 6, 8, 24, and 48 hours). For the isotherm study, the Bis-GMA/FA were immersed in 20 mL of different concentrations of formaldehyde (2, 4, 6, 8, 10, 12, 14, 16, 18, and 20 mgL^{-1}) for 8 hours. The same procedure was followed for the mixture with Fluoral-P reagent and the

measurement of absorbance intensity. The kinetics of the adsorbent material depends on the surface area of the adsorbed Bis-GMA/FA. Pseudo-first-order (Eq. 1) and pseudo-second-order (Eq. 2) kinetic models of the adsorbed surface were applied to fit experimental data and verify the nature of the adsorbent material on Bis-GMA/FA. Equations are given as follows [9]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

Where: q_t, q_e, k_1 and k_2 are the adsorption capacity (mgg^{-1}) at any time (hours), the adsorption capacity (mgg^{-1}) at equilibrium, pseudo-first-order adsorption rate constant (min^{-1}), and pseudo-second-order adsorption rate constant ($mgg^{-1}min^{-1}$), respectively [10]. The specificity of an imprinted polymer and non-imprinted polymer to template molecule was estimated using an imprinting factor (IF). The IF can be determined from Equation (3). The target partition coefficient K_{MIP} and K_{NIP} is determined from Equation (4). Where C_F is the amount of formaldehyde bound to MIP or NIP and C_S is the concentration of the free template residue in the solution [11].

$$IF = \frac{K_{MIP}}{K_{NIP}} \quad (3)$$

$$K = \frac{C_F}{C_s} \quad (4)$$

The experimental isotherm data that was developed to evaluate adsorption properties by Langmuir and Freundlich described the equations of adsorption isotherms. These equations are usually used to describe adsorption equilibrium for formaldehyde treatment applications in solutions.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{k_L q_{max}} \quad (5)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (6)$$

Where, q_e and q_{max} are the equilibrium and maximum uptake capacities (mgg^{-1}) after adsorption in solution, respectively. C_e is the formaldehyde concentration (mgL^{-1}) after adsorption in solution at equilibrium, b represents the Langmuir adsorption constant. k_f is the Freundlich constant related to adsorption uptake capacities (mgg^{-1}), while n represents the adsorption intensity or a measure of surface heterogeneity. Its value gets between 0 and 1.

Results and Discussion

Synthesis and Characterization of Bis-GMA/FA

The photopolymerization process of the reaction begins with the product generating free radicals from the initiator (CQ) in the presence of the reaction accelerator (EDMAB). Therefore, upon crosslinking with (TEGDMA), solid MIPs were formed containing template molecules (CH_2O), which provides mechanical and morphological stability to the MIPs matrix before and during the photopolymerization process [12]. During the polymerization process, imprinted cavities were created inside the solid MIPs that were the same size and shape as the template molecules (CH_2O) revealed after the washing process. Figure 1 depicts the interaction of a polymer's functional group with a template (formaldehyde). The presence of oxygen-containing groups (carbonyl, ether, and alcohol) in the polymer is responsible for molecular interaction during formaldehyde recognition [1].

Figure 2 shows the FTIR spectrum of Bis-GMA/FA before and after the washing stage. The spectrum was also compared with Bis-GMANIP (non-imprinted). The FTIR spectra of the Bis-GMA/FA before the washing stage showed a broad peak at the 1650 – 1750 cm^{-1} region, which is attributed to the extra carbonyl groups (band of C=O). This broad peak indicates the presence of a template (formaldehyde) in Bis-GMA/FA, but it becomes sharp and not broad after washing processes, which is similar to the spectrum of Bis-GMANIP. The finding in Tang et al. (2017) also demonstrate that the FTIR spectrum of MIP after formaldehyde removal has similar spectrum with the NIP [7]. The presence of carbonyl groups in aldehydes and ketones was indicated by the strong absorption peak at 1720 cm^{-1} [13]. Near 3289 cm^{-1}, a strong band of O-H stretching absorbs for Bis-GMA and PVA. The strong absorption band at 2900 cm^{-1} is due to (C-H stretching) in Bis-GMA and TEGDMA. The peaks that absorb near 1421 cm^{-1} correspond to vibrations caused by the presence of C–O stretching.

The surface morphology (pellet surface) of Bis-GMA/FA and Bis-GMANIP are shown in Figure 3. Bis-GMA/FA (after washing) appear to have clearly visible rough and porous surface compared to Bis-GMANIP and Bis-GMA/FA (before washing) due to the presence of cavities and porosity caused by the removal of templates from Bis-GMA/FA after washing [14]. This attributed to the establishment of formaldehyde recognition sites.

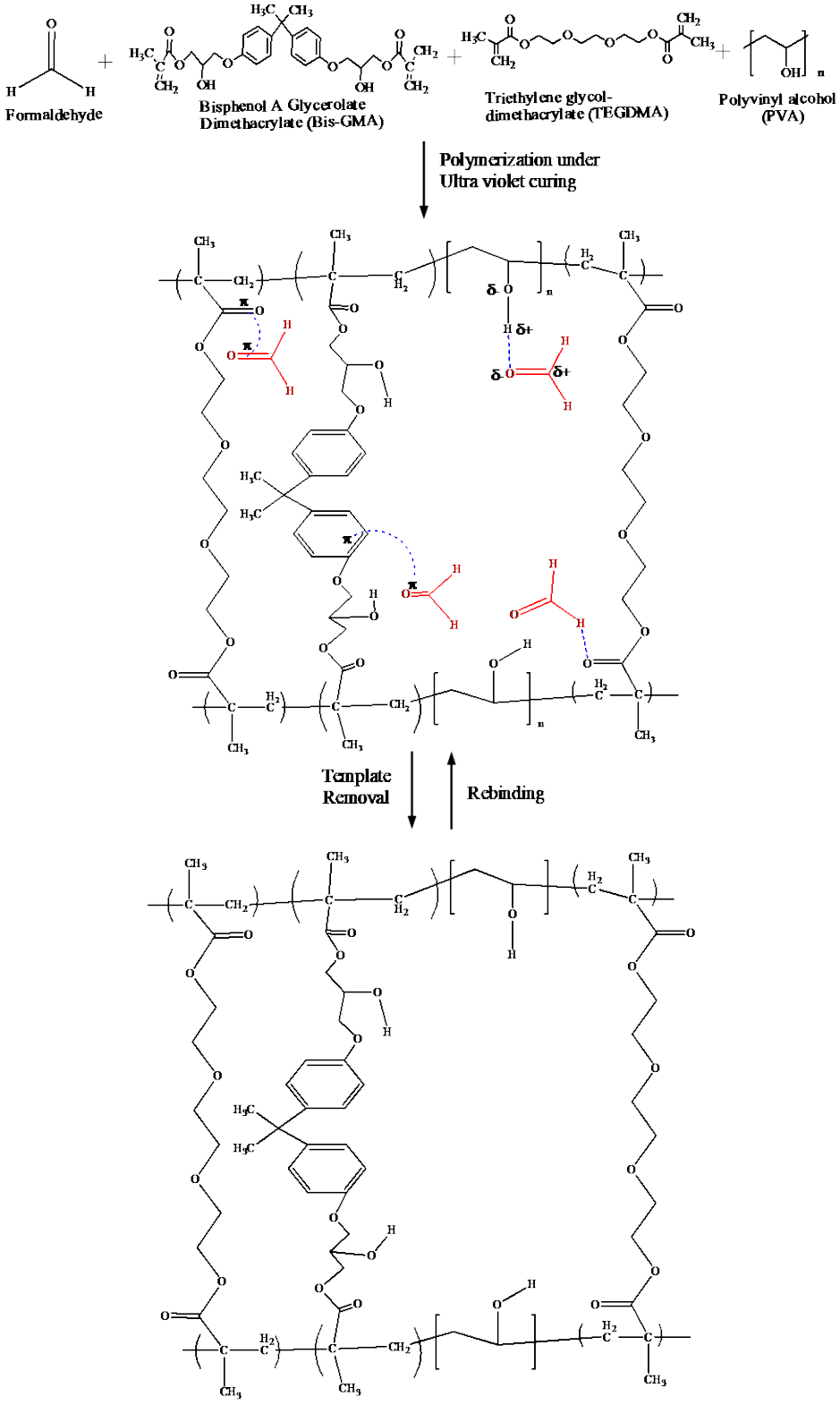


Figure 1: The possible molecular interaction of a functional group of polymer with a template (formaldehyde) during synthesis and recognition study

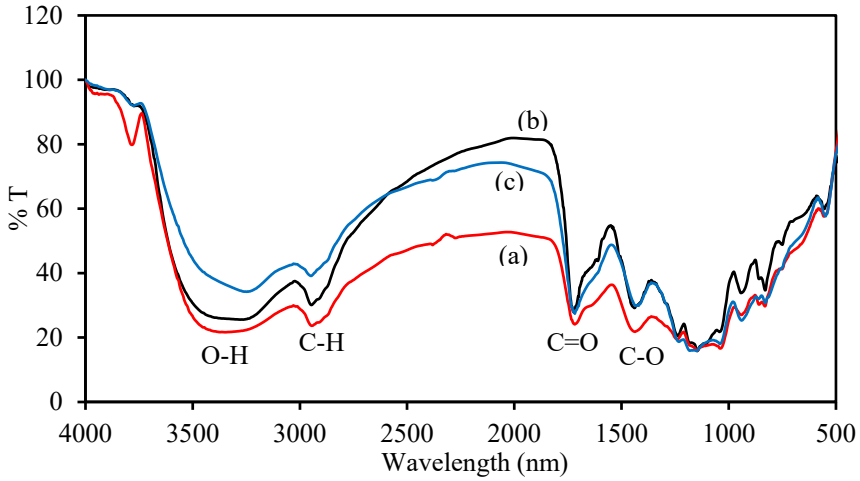


Figure 2: The FTIR spectrum of (a) Bis-GMA/FA before washing, (b) Bis-GMA/FA after washing and (c) Bis-GMANIP

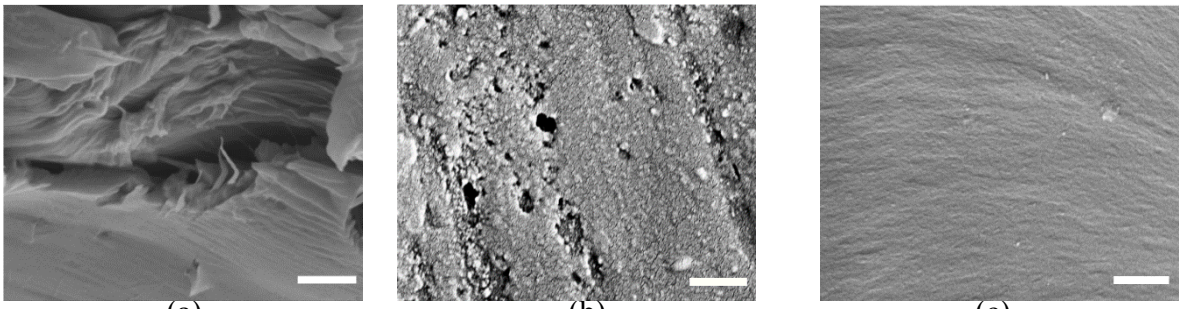


Figure 3: FESEM micrographs of (a) Bis-GMA/FA before washing, (b) Bis-GMA/FA after washing and (c) Bis-GMANIP

The Reaction of Formaldehyde and Fluoral-P

The reaction of remaining formaldehyde in solution with Fluoral-P was carried out in phosphate buffer pH 7. This reaction will produce 3,5-diacetyle-1,4-dihydrolutidine (Figure 4) [8]. The absorbance intensity of the reaction product, 3,5-diacetyle-1,4-dihydrolutidine, was measured at 412 nm using an Agilent ultraviolet spectrophotometer. A colour change from light yellow to yellowish-green occurs during the reaction, indicating the complex formation between Fluoral-P and formaldehyde [8].

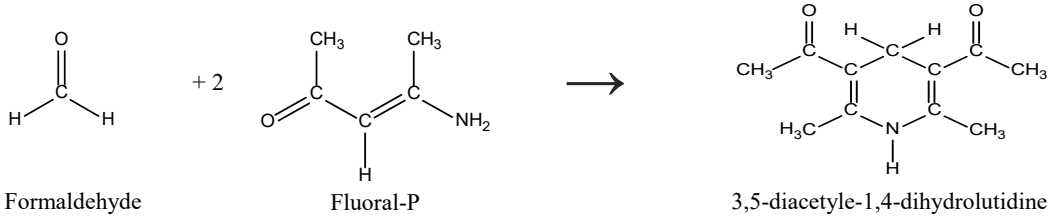


Figure 4: Reaction between formaldehyde and Fluoral-P to produce 3,5-diacetyle-1,4-dihydrolutidine [8]

The Recognition Studies of Formaldehyde onto Bis-GMA/FA

a) The effect of pH and monomer ratio

Figure 5 shows the effect of pH solution against the formaldehyde adsorption onto Bis-GMA/FA in an aqueous solution. The formaldehyde uptake on Bis-GMA/FA increased in acidic media until it reached the highest uptake at pH 7, then the uptake decreased in the basic medium (> pH7). The highest formaldehyde uptake occurs at low pH due to more attractive forces between adsorbent and formaldehyde caused by the accumulation of positively charged hydrogen ions around the adsorbent surface, whereas at basic pH (>pH 7), formaldehyde uptake decreases due to the repulsion of the accumulation of negatively charged hydroxyl ions around the adsorbent surface, providing repulsive forces for the formaldehyde carbonyl group [2,15]. The pH of the solution is considered a significant factor influencing the adsorption properties of formaldehyde on polymers because it regulates the electrostatic interaction between the target molecule and polymer [16].

The rebinding study of formaldehyde on the Bis-GMA/FA with different ratios of monomer is shown in Figure 6. The results revealed that Bis-GMA/FA with a ratio of 1 has the highest uptake when compared to the others. Notably, Bis-GMA/FA prepared with different functional monomer/cross-linker ratios had a significantly higher affinity with these substances' binding properties to the target molecule due to its diverse structural properties [17]. The lower binding capacity (ratio > 1) attributed to the loss of rigidity and selectivity of the polymers [18].

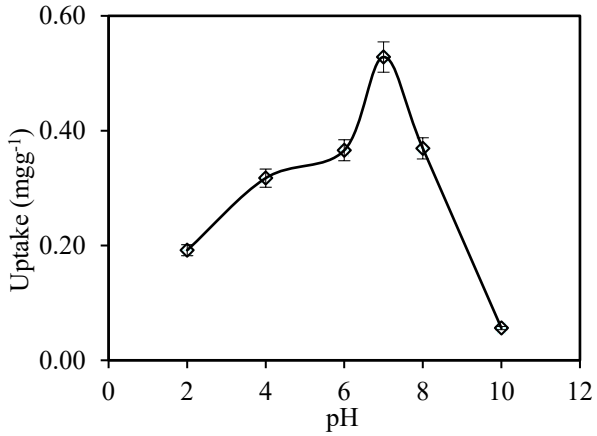


Figure 5: Effect of pH for formaldehyde uptake onto Bis-GMA/FA in aqueous solution

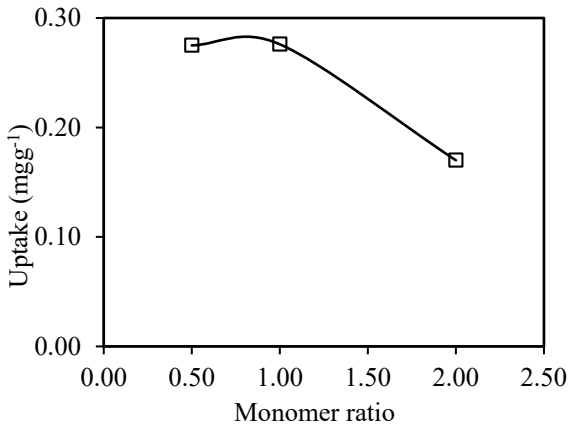


Figure 6: The optimum ratio of Bis-GMA/FA for the adsorption of formaldehyde in aqueous solution

b) The effect of template percentage in Bis-GMA/FA, equilibrium time and initial concentration.

Figure 7 shows that Bis-GMA/FA with 0.1 % template has higher uptake and binding capacity for formaldehyde than other Bis-GMA/FA. The binding capacity for template molecule adsorption is an important parameter for evaluating the best MIPs. The binding capacity increased rapidly and reached the highest uptake at 0.1 % before decreasing irregularly. This occurrence trend demonstrated that the binding sites were fully saturated, preventing template molecules from implanting into the binding sites of Bi-GMA/FA, as well

as the lack of free binding sites. This is consistent with the findings of Shafqat et al [6]. The rebinding of formaldehyde onto Bis-GMA/FA was done at several time intervals with three different concentrations (5, 10, 20 mgL^{-1}). Figure 8 shows the equilibrium steady-state time of formaldehyde adsorption onto Bis-GMA/FA in an aqueous medium. Within eight hours, the adsorption had reached equilibrium. The initial formaldehyde concentration does not affect the steady-state equilibrium time. The time required for optimum adsorption was determined to be an equilibrium steady state time of eight hours.

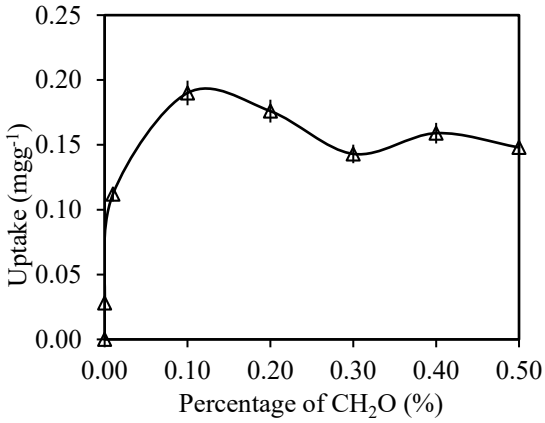


Figure 7: Optimum uptake of formaldehyde onto Bis-GMA/FA with different percentages of CH_2O (%)

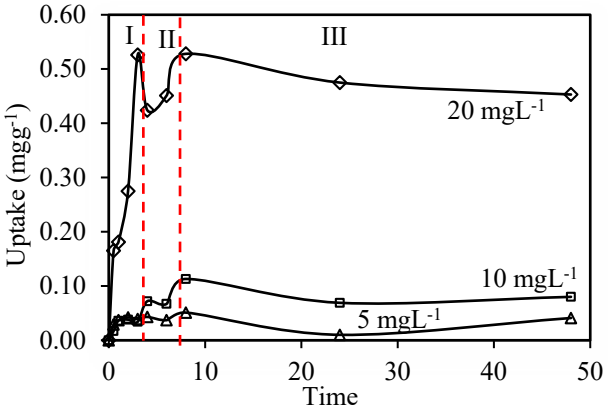


Figure 8: The effect of initial concentration of formaldehyde onto Bis-GMA/FA in aqueous solution

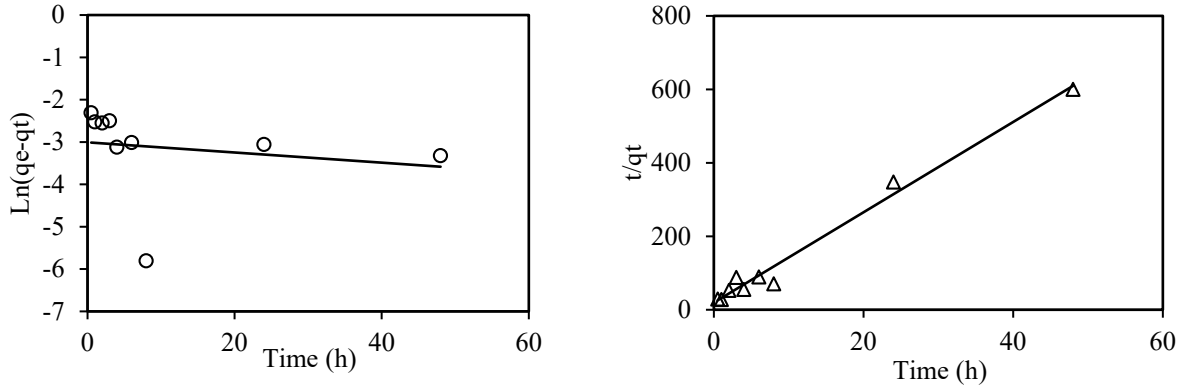
The uptake of formaldehyde increases with time in the first section (I) due to the cavities' ability on the polymer's surface to adsorb formaldehyde. In contrast, in the second section (II), the uptake of formaldehyde decreases due to internal pressure inside the internal pores that inhibits the formaldehyde molecules from entering the pores. The uptake of formaldehyde is constant in the third section (III), indicating that all of the vacant/binding sites on the Bis-GMA/FA have been fully occupied. Bis-GMA/FA showed a higher binding affinity (higher IF value, IF=1.01) for formaldehyde as compared to Bis-GMANIP, this indicates that specific binding sites on the Bis-GMA/FA could be the most important part in the process of recognizing a target (Table 1). The higher IF value demonstrated that Bis-GMA/FA prepared with formaldehyde as a template molecule has high specificity and re-binding ability [7].

Table 1: The imprinting Factor (IF) of Bis-GMA/FA and Bis-GMANIP

Polymer	K	IF
Bis-GMA/FA	0.3646	1.01
Bis-GMANIP	0.3613	0.99

Figure 9 shows the pseudo kinetic model for the adsorption of formaldehyde onto Bis-GMA/FA. The correlation coefficients values (R^2) of Bis-GMA/FA obtained for pseudo-first-order (k_1) and pseudo-second-order (k_2) models were 0.031 and 0.984, respectively, as shown in Table 2. The results indicate that the adsorption of formaldehyde onto Bis-GMA/FA fitted well with a pseudo-second-order. Therefore, it is possible to control the

adsorption behavior by a certain chemical adsorption mechanism. The same trend has been reported by Xu et al. (2020) in kinetic studies [19].



(a) Pseudo-first order (b) Pseudo-second order

Figure 9: Kinetic model of (a) pseudo-first and (b) pseudo-second for the adsorption of formaldehyde onto Bis-GMA/FA in an aqueous solution

Table 2: Adsorption kinetic parameters for formaldehyde onto the Bis-GMA/FA

Pseudo-first order			**Pseudo-second order**		
q_e (mgg^{-1})	k_1 (min^{-1})	R^2	q_e (mgg^{-1})	k_2 ($mgg^{-1}min^{-1}$)	R^2
0.05	0.012	0.031	0.081	7.81	0.984

The Isotherm Studies of Formaldehyde onto Bis-GMA/FA

The formaldehyde adsorption mechanism of these solutions was investigated using isotherm models. The adsorption data were plotted and calculated according to the linear forms, Langmuir (Eq. 5) and Freundlich (Eq. 6) isotherms, respectively. The adsorption of formaldehyde onto Bis-GMA/FA does not fit the Langmuir isotherm well (R^2 = 0.346) (Figure 10), but it does fit the Freundlich isotherm well (R^2 = 0.863) (Figure 11). The values of k_f and n obtained indicate that the adsorption on the surface is heterogeneous [20], and the fact that the parameter n (Table 3) is close to 1 indicates that the heterogeneity of Bis-GMA/FA and formaldehyde in an aqueous medium is good. As a result, the Freundlich isotherm was chosen as the best model to describe the adsorption of formaldehyde onto Bis-GMA/FA.

The imprinted site of formaldehyde molecules and interaction of π- π/dipole-dipole/hydrogen bonding of O-H, C=O, and C-O group on the surface of Bis-GMA/FA with the acidic carboxylic groups of formaldehyde is responsible for the formaldehyde rebinding on Bis-GMA/FA. The cooperative interaction of dipole-dipole interaction and hydrogen bonding of carbon microspores surface with the acidic carboxylic groups of formaldehyde plays an essential role in formaldehyde adsorption on carbons. Furthermore, the oxygen-containing groups on the surface of Bis-GMA/FA play a vital role in formaldehyde removal [1]. Bis-GMA/FA can recognize formaldehyde molecules and thus improve adsorption uptake. The rebinding of formaldehyde onto Bis-GMA/FA in an aqueous solution was aided by the favourable adsorption with a heterogeneity index close to one. This non-covalent

approach (self-assembly) takes place between the hydroxyl group of the monomer (Bis-GMA) and the carbonyl group (C=O) of the template (CH_2O), which is a well-accepted hydrogen bond donor (O-H) group and serves as the driving force betweenthe functional monomer (the hydroxyl group of the monomer) and the target molecule (the carbonyl group of formaldehyde) for the molecular recognition ability, which controls the rebinding process [21].

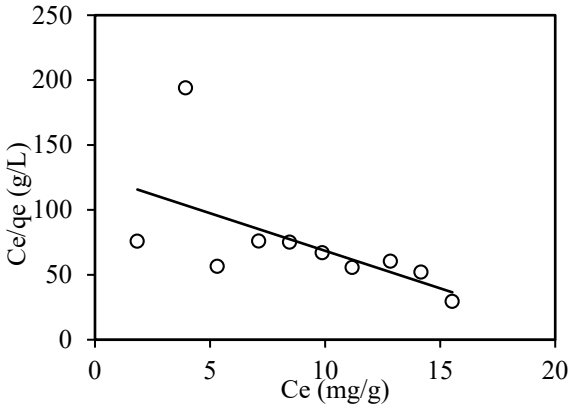


Figure 10: Langmuir isotherms model plot analysis for formaldehyde binding properties to the Bis-GMA/FA

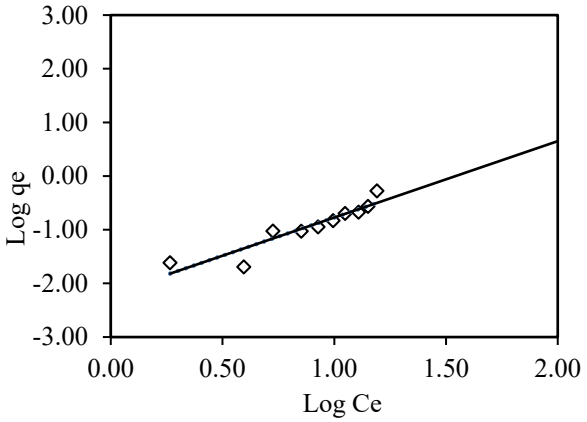


Figure 11: Freundlich isotherms model plot analysis for formaldehyde binding properties to the Bis-GMA/FA

Table 3: Isotherms parameters of formaldehyde onto Bis-GMA/FA in an aqueous solution

Langmuir			**Freundlich**		
k_L	q_{max}	R^2	k_f	n	R^2
- 0.045	- 0.172	0.346	0.006	0.702	0.863

Conclusions

Bis-GMA/FA was successfully photopolymerized with imprinted formaldehyde molecules and displayed great recognition property towards formaldehyde in an aqueous medium. Compared to Bis-GMANIP, Bis-GMA/FA showed the presence of cavities or pores on the surface of the polymer and provided advantages in recognition and adsorption uptake towards formaldehyde. It was firmly believed that the recognition and rebinding of formaldehyde onto Bis-GMA/FA01 occurred via π- π, dipole-dipole and hydrogen bonding O-H, C=O, and C-O groups on the surface of Bis-GMA/FA with the acidic carboxylic groups of formaldehyde.

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Author contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of conflict of interest

The authors have no disclosures to declare.

Compliance with ethical standards

The work is compliant with ethical standards.

References

[1] Wang, J. & Tao, Y. (2020). Removal of Formaldehyde from the Indoor Environment Using Porous Carbons and Silicas. *Recent Innovation in Chemical Engineering (Formerly Recent Patents on Chemical Engineering)*, 13(3), 194 – 202.

[2] Salman, M., Athar, M., Shafique, U., Rehman, R., Ameer, S., Ali, S. Z. & Azeem, M. (2012). Removal of Formaldehyde from Aqueous Solution by Adsorption on Kaolin and Bentonite: A Comparative Study. *Turkish Journal of Engineering and Environmental Sciences,* 36(3), 263 – 270.

[3] Ayadi, C., Anene, A., Kalfat, R., Chevalier, Y. & Hbaieb, S. (2019). Molecularly Imprinted Polyaniline on Silica Support for the Selective Adsorption of Benzophenone-4 from Aqueous Media. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 567, 32 – 42.

[4] Udayakumar, M., El Mrabate, B., Koós, T., Szemmelveisz, K., Kristály, F., Leskó, M., Filep, A., Géber, R., Schabikowski, M., Baumli, P., Lakatos, J., Tóth, P. & Németh, Z. (2021). Synthesis of Activated Carbon Foams with High Specific Surface Area Using Polyurethane Elastomer Templates for Effective Removal of Methylene Blue. *Arabian Journal of Chemistry.* 14(7), 103214, 1 – 18.

[5] Azizi, A., Shahhoseini, F. & Bottaro, C. S. (2020). Magnetic Molecularly Imprinted Polymers Prepared by Reversible Addition Fragmentation Chain Transfer Polymerization for Dispersive Solid Phase Extraction of Polycyclic Aromatic Hydrocarbons in Water. *Journal of Chromatography A*, 1610, 460534, 1 – 15.

[6] Shafqat, S. R., Bhawani, S. A., Bakhtiar, S. & Ibrahim, M. N. M. (2020). Synthesis of Molecularly Imprinted Polymer for Removal of Congo Red. *BMC Chemistry,* 14(27), 1 – 15.

[7] Tang, X., Raskin, J. P., Lahem, D., Krumpmann, A., Decroly, A. & Debliquy, M. (2017). A Formaldehyde Sensor Based on Molecularly-Imprinted Polymer on a TiO_2 Nanotube Array. *Sensors*, 17(4), 675, 1 – 15.

[8] Loh, H. C., Chong, K. W. & Ahmad, M. (2007). Quantitative Analysis of Formaldehyde Using UV-VIS Spectrophotometer Pattern Recognition and Artificial Neural Networks. *Analytical Letters,* 40(2), 281 – 293.

[9] Madikizela, L. M., Zunngu, S. S., Mlunguza, N. Y., Tavengwa, N. T., Mdluli, P. S. & Chimuka, L. (2018). Application of Molecularly Imprinted Polymer Designed for the Selective Extraction of Ketoprofen from Wastewater. *Water SA,* 44(3), 406 – 418.

[10] Zhao, X., Mai, Y., Chen, D., Zhang, M. & Hu, H. (2019). Selective Enrichment of Clenbuterol onto Molecularly Imprinted Polymer Microspheres with Tailor-Made Structure and Oxygen Functionalities. *Polymers*, 11(10), 1635, 1 – 22.

[11] Yu, H., He, Y., She, Y., Wang, M., Yan, Z., Ren, J. H., Caoa, C., Shaoa, Y., Wanga, S., Abd El-Atyd, A.M., Hacımüftüoğlue, A. & Wang, J. (2019). Preparation of Molecularly Imprinted Polymers Coupled with High-Performance Liquid Chromatography for the Selective Extraction of Salidroside from Rhodiola Crenulata. *Journal of Chromatography B*, 1118 – 1189, 180 – 189.

[12] Paruli, E. I., Soppera, O., Haupt, K. & Gonzato, C. (2021). Photopolymerization and Photostructuring of Molecularly Imprinted Polymers. *ACS Applied Polymer Materials,* 3(10), 4769 – 4790.

[13] Solomons, T. G., Fryhle, C. B. & Snyder, S. A. (2016). *Organic Chemistry, 12e Binder Ready Version Study Guide & Student Solutions Manual*. 12th edition (John Wiley & Sons) pp. 711 – 760.

[14] Wang, D., Yang, Y., Xu, Z., Liu, Y., Liu, Z., Lin, T., Chen, X. & Liu, H. (2021). Molecular Simulation-Aided Preparation of Molecularly Imprinted Polymeric Solid-Phase Microextraction Coatings for Kojic Acid Detection in Wheat Starch and Flour Samples. *Food Analytical Methods*, 14(10), 2076 – 2087.

[15] Zahed, M., Jafari, D. & Esfandyari, M. (2020). Adsorption of Formaldehyde from Aqueous Solution Using Activated Carbon Prepared from Hibiscus Rosa-Sinensis. *International Journal of Environmental Analytical Chemistry,* 102(13), 1 – 23.

[16] Ma, X., Li, M., Zhang, J., Wang, R. & Jin, S. (2021). Recognition and Selective Extraction of Poly-Γ-Glutamic Acid Based on Molecular Imprinting Technology. *International Journal of Biological Macromolecules,* 172, 1 – 9.

[17] Brilliantova, I. S., Lebedev, I. V., Gordienko, M. G. & Menshutina, N. V. (2019). Synthesis and Analysis of Silica–Resorcinol–Formaldehyde Aerogels. *Russian Journal of Physical Chemistry B,* 13(7), 1174 – 1181.

[18] Yoshimatsu, K., Yamazaki, T., Chronakis, I.S. & Ye, L. (2012). Influence of Template/Functional Monomer/Cross-Linking Monomer Ratio on Particle Size and Binding Properties of Molecularly Imprinted Nanoparticles. *Journal of Applied Polymer Science,* 124(2), 1249 – 1255.

[19] Xu, L., Zhao, Z. X., Huang, Y. A. & Zhu, Q. J. (2020). Preparation of Chitosan Molecularly Imprinted Polymers and the Recognition Mechanism for Adsorption of Alpha-Lipoic Acid. *Molecules*, 25(2), 312, 1 – 15.

[20] Ayawei, N., Ebelegi, A. N. & Wankasi, D. (2017). Modelling and Interpretation of Adsorption Isotherms. *Journal of Chemistry*, 2017, 1 - 11.

[21] Daniels, E., Mustafa, Y. L., Herdes, C. & Leese, H. S. (2021). Optimization of Cortisol-Selective Molecularly Imprinted Polymers Enabled by Molecular Dynamics Simulations. *ACS Applied Biomaterials,* 4(9), 7243 – 7253.