Australian Journal of Basic and Applied Sciences, 10(18) December 2016, Pages: 346-353

AUSTRALIAN JOURNAL OF BASIC AND APPLIED SCIENCES

ISSN:1991-8178 EISSN: 2309-8414
Journal home page: www.ajbasweb.com

Application of Taguchi method for removal of Benzo(a)pyrene by exploiting Carboxymethyl β-Cyclodextrin in molecular imprinting polymer technique

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ARTICLE INFO

Article history:
Received 6 October 2016
Acceptance 15 November 2016

Keywords:
Surface molecular imprinting technique, Molecular recognition, Taguchi method, PAHs and Benzo (a) Pyrene.

ABSTRACT

The molecularly imprinted polymer (MIP) based on styrene and carboxymethyl β-cyclodextrin as monomer and EGDMA as the cross-linker were synthesized in the bulk polymerization process for the purpose of selective recognition of benzo(a)pyrene (BaP). The prepared polymer was characterized using the Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM), and ^{1}H-NMR. The Taguchi experimental design method was applied for is used to identify the factors and their interactions. The removal percent of benzo(a)pyrene (BaP) compound in this process was greatly influenced by factors such as pH, catalyst dose and concentration. By using orthogonal experimental design and analysis technique, the performance of this process can be analyzed with more objective conclusion through only a small number of simulation experiments. Analysis of variance (ANOVA) was carried out to identify the significant factors affecting the response and the best possible factor level combination was determined through.

INTRODUCTION

The technique of molecular imprinted polymers (MIPs), introduced in 1972 by Wulff and Sarhan (1972), has been shown to be capable of producing materials with ‘‘antibody-like’’ selectivity (Tarbin, J.A., M. Sharman, 2001), where monomers and cross-linkers are copolymerized in the presence of a template molecule. The removal of the template molecule from the obtained polymer by simple solvent extraction reveals the complementary binding sites that recognize the template molecule from its structurally similar compounds (Huang, J.T., *et al*., 2004; Tamayo, F.G., *et al*., 2005; Guo, T.Y., *et al*., 2004; Shi, H.Q., *et al*., 1999; Hosoya, K., *et al*., 1996; Piletsky, S.A., *et al*., 1995). Due to their high mechanical and chemical stabilities, ease of preparation, and suitability for a wide range of operating conditions, molecularly imprinted polymers (MIPs) have been developed in various fields, such as solid phase extraction (Puoci, F., *et al*., 2007), chromatographic separation (Huang, X., *et al*., 2003), catalysis (Lakshmi, D., *et al*., 2009), membranes (Hillberg, A.L., *et al*., 2009), and sensors (Antwi-Boampong, S., *et al*., 2014). However, conventional MIPs have low capacity and poor site accessibility for template molecules. To overcome this limitation, an appropriate modification of the monomer with β-cyclodextrin (β-CD) has been made to improve the binding capacity of the MIP (Sreenivasan, K., 1996). β-cyclodextrin (β-CD) is a cyclic oligosaccharide, consisting of seven glucose unit residues linked with α-(1,4) bonds, which has the primary hydroxyl groups on the narrow (primary) side, and the secondary hydroxyl on the inner cavity, as well as a hydrophilic external surface. Due to its unique structure of a truncated cone-shaped molecule, it ideally forms an inclusion compound with various analytes by “host-guest interaction”

To Cite This Article: Hager R. Ali., Application of Taguchi method for removal of Benzo(a)pyrene by exploiting Carboxymethyl β-Cyclodextrin in molecular imprinting polymer technique. ***Aust. J. Basic & Appl. Sci.,*** *10(18): 346-353, 2016*

(Tang, S., *et al*., 2006). Hence, the orientation of the β-CD molecule residues in the MIPs is suitable for the cooperative binding of the templates (Xu, Z., *et al*., 2007). The preparation of β-CD-MIPs has previously been reported to be successful (Akiyama, T., *et al*., 2001; Asanuma, H., *et al*., 2001; Hishiya, T., *et al*., 2002). The modification of the monomer with β-CD is a promising step, as there is a lack of specific binding sites in the cavities created by imprinting. By linking several functional groups of monomer to β-CD, the recognition ability could be improved, which increases the binding capacity of MIPs (Ma, X., *et al*., 2013). CD and its derivates contained a relatively hydrophobic cavity; therefore, it can be used as the molecular recognizer through host-guest interactions. A group of important contaminants such as polycyclic aromatic hydrocarbon (PAHs) (Xu, Z.F., *et al*., 2013), polycyclic aromatic hydrocarbons (PAHs), a group of highly lipophilic organic compounds, have caused increasing attention in recent years because of their carcinogenicity and iniquitousness in the environment. Advanced technology for measuring environmental contamination in water sources, coupled with recent developments in health science has determined restrictions and set limits for levels of these compounds in water. The permitted concentration of PAHs in drinking water is limited to is 3 mg/L (Hosoya, K., *et al*., 1996). Benzo[a]pyrene (BAP) is one of the best known carcinogenic PAH and is also considered to act as an endocrine disrupting chemical (EDC). It is generally formed by incomplete combustion and pyrolysis of organic materials. It also has been detected in tobacco smoke, sediment, soils, water, air, marine organisms and even foodstuffs (Kanchanamayoon, W., N. Tatrahunl, 2008; Baklanov, A., *et al*., 2007). Therefore, BAP is frequently used as an indicator of the presence of PAHs. Numerous investigators are interested in the development of analytical methods for separation and measurement of this analyte. For process optimization, the Taguchi method is commonly adopted because it can significantly reduce the overall testing time and cost. It uses a specially designed orthogonal array, consisting of controllable factors and their variation levels, to optimize the experimental conditions, Taguchi (Latimer, J., J. Zheng, 2003). Taguchi method is a multi-parameter optimization procedure, which is very useful in identifying and optimizing dominant process parameters with a minimum number of experiments (Roy, R.K., 1990). This technique is based on an OA of experiments and includes data transformation into an accurate and desirable signal to- noise (S/N) ratio (Taguchi, G. and Y. Wu, 1979). An OA is a minimal set of experiments with various combinations of parameter levels. The selection of a suitable OA depends on the number of control factors and their levels (Logothetis, N., 1997). The optimization of the observed values is determined by using the signal-to-noise (S/N) ratios and analysis of variance (ANOVA). In this work, the (MIP/CMCD) molecular imprinted polymer based on carboxymethyl-b-cyclodextrin as monomer have been fabricated successfully with co-precipitation method which could be used in adsorption efficiently and repeatedly. These polymers used as site-specific adsorbents of benzo(a)pyrene (BaP). The effect of experimental parameters such as initial concentration, dose and solution pH on removal was investigated using an L9 orthogonal array. The Taguchi experimental design has been used to determine the optimum conditions for the maximum removal of the BaP from aqueous solutions.

Experimental Section:

i- *Reagents and chemicals:*

Benzo(a)pyrene (BaP) (98%), ethylene glycol dimethacrylate (EGDMA) (98%), b-cyclodextrin, mono chloroacetic acid, dichloromethane, glacial acetic acid, methanol (MeOH) and benzoyl peroxide were all purchased from the Sigma Chemical Company.

ii- *Synthesis of carboxymethyl-beta-cyclodextrin (CMCD):*

Carboxymethyl-beta b-cyclodextrin (CMCD) was prepared by the following procedure**:** A mixture of beta-cyclodextrin (β-CD) (10 grams, 8.818 mmol) and NaOH (9.3 grams, 232.5 mmol) was treated with a-27-ml volume of mono chloroacetic acid (16.5% w/w). The mixture was reacted at 50^0C for 5 hours. Then, the reaction product was cooled to room temperature and the pH was adjusted to neutral (6 to 7) using HCl. The neutral solution was filtered to separate salt containing in it. The solution was poured to a superfluous methanol solvent to produce a white precipitation. The solid precipitation was filtered and dried under vacuum. Then, it was crushed with an addition of acetone.

iii- *Preparation of MIP/CMCD:*

A typical procedure for preparing MIP/CMCD is as follows: The BaP (0.0155 gm, 0.06 mmol), Carboxymethyl b-cyclodextrin 0.1 gm and styrene (0.2083, 2 mmol) were dissolved in 10mL of dichloromethane. The mixture stirred for 2hours to make intensive mixing. Then EGDMA (7.9 gm, 40 mmol) and benzoyl peroxide (0.122 g, 0.5 mmol) were successively added to the solution under a nitrogen atmosphere for 20 min. After mixing, the pre-polymerized mixture was then polymerized by thermal initiation at 80^oC for overnight. The resultant powder was coded (MIP/CMCD+BaP). The freed BaP in the formed gel were continuously extracted and washed with methanol/acetic acid (9:1, v/v) until BaP was detected by the HPLC Analysis Instrument. The obtained MIP/CMCD was dried overnight for further investigation; the product was denoted as MIP/CMCD-BaP.

Characterization of the prepared materials:

The structure of adsorbents was investigated by the FTIR spectrum in the 4000-400 cm^{-1} range was recorded for the prepared samples at room temperature by Perkin Elmer (model spectrum one FT-IR spectrometer, USA). Samples were prepared using the standard KBr pellets.

The morphology of the samples was imaged using transmission electron microscope (Tecni G20, FEI, Netherland) and a scanning electron microscopy Quanta 250 FEG (FEI, Netherland) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V. magnification14x up to 1000000 and resolution for Gun.1n).

The HNMR spectrum was measured on a Varian Gemini-200 MHz NMR spectrometer at Laser Unit, Physics Department, Faculty of Science, Cairo University, Cairo, Egypt.

Design of experiments (DOE):

The Taguchi method, a powerful tool for design of experiments, was applied to determine the optimum number of the experiments (Baklanov, A., *et al.*, 2007). This technique includes data transformation to a signal-to-noise (S/N) ratio, which is a measure of the variations presented, and the larger the S/N ratio, the more important the factors and the better the results (Taguchi, G. and Y. Wu, 1979). The experiments were performed using solutions of 10 mL of BaP solution was introduced into 20 ml flasks with temperature controlled shaker at a constant speed of 200 rpm. Experiments were performed using solutions of BaP at different dose (1, 3, 5 g), pH (2, 7, 9) and concentration of BaP (5, 10, 25 ppm). The contents of the flasks were equilibrated on the shaker at 25 ^{o}C for 3 h. The factors and their assigned levels are presented in Table 1. The Taguchi L9 orthogonal array for this set of parameters is shown in Table 2. For analysis of the results and optimization of the conditions, Minitab software (Version 17) was used and the efficiency was reported as the% degradation. An HPLC instrument model Agilent 1200 series with a 5 µm×25.0 cm×4.6 mm LC -C18 column and equipped with PDA detector and auto-sampler was used to follow up the degradation reaction. The mobile phase consisted of 40% water and 60% acetonitrile. The solvent program was isocratic, the flow rate was 1.0 ml min^{-1} and the injection volume was 5 µl and the removal efficiency (RE) was determined as follows (Eq. 1):

$$RE = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \qquad (1)$$

Table 1: Factors and their levels for design of experiments

Symbol	Factors	Level		
		1	2	3
A	pH	2	7	9
B	Dose (g)	1	3	5
C	Concentration (mg/l)	5	10	25

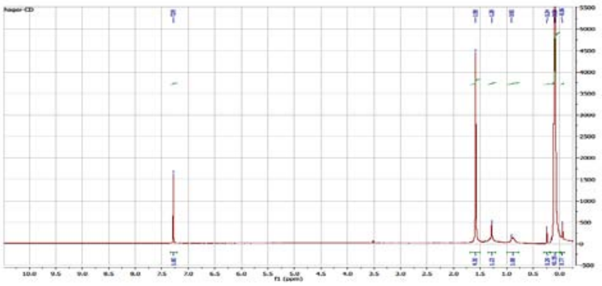
Table 2: An orthogonal array of L9 for experiments

Experimental No.	A	B	C	% Degradation	S/N Ratio
1	1	1	1	61	35.7066
2	1	2	2	62	35.5630
3	1	3	3	60	35.5630
4	2	1	2	61	35.7066
5	2	2	3	63	35.4170
6	2	3	1	64	36.1236
7	3	1	3	65	35.2686
8	3	2	1	63	36.3909
9	3	3	2	66	35.8478

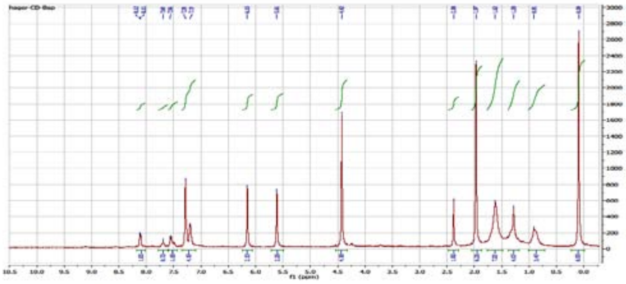
RESULTS AND DISCUSSION

Characterization of the prepared polymer:

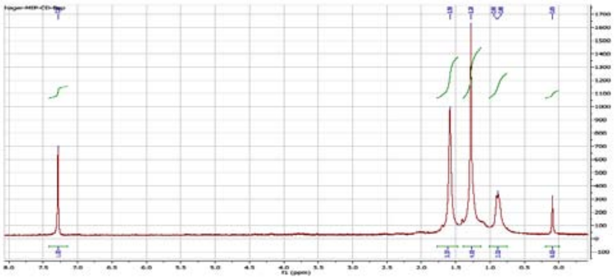
Direct evidence for the formation of inclusion complex can be obtained from H NMR [29]. It can be seen from Fig (1) the H-NMR spectrum of compound in the DMSO solvent, the single peaks of chemical shift at 1.51 ppm and 1.25 ppm are carboxymethyl, 0.25 and 1.77ppm for methylene protons and 0.5-1.0 ppm for methyl proton. The ^{1}H-NMR spectrum revealed the resonances characteristic of the benzo(a)pyrene between 7-8.2 ppm. The signals in the regions of 1.89 ppm for CH_3 are related to EGDMA. However, from the NMR spectrum of the vinyl of styrene the sharp signal at 4.5 ppm is ascribed to the methylene protons in the polymer. The structural formation of the copolymer can be simply determined by reducing the intensity of the vinyl peaks at 5.6 and 6.2 ppm in the copolymer spectrum, when benzo(a)pyrene ring entered into the hydrophobic cavity of CD, the change of the micro-environment leaded the phenyl ring proton signals split in the region of 7-7.5 ppm.



CMCD



MIP/CMCD+BaP



MIP/CMCD-BaP

Fig. 1: HNMR of the prepared materials

FTIR spectra of CMCD, MIP/CMCD+Bap and MIP/CMCD-BaP are demonstrated in Fig.(2). Stretching peaks at 1140 and 1730 cm^{-1} corresponds to C–O and C=O in EGDMA, respectively. The original cross-linking agent EGDMA and styrene have abundant vinyl groups. However, the characteristic C=C peaks at 1630, 990, and 910 cm^{-1} show low intensity that verified the crosslinking polymerization reaction. Additionally, flexions at 700–1000 cm^{-1} corresponding to aromatic C–H bond can be seen in the spectra. Peaks observed at 1313, 1185 and 1046 cm^{-1} related to the =C–H in-plane vibration and the =C–H out-of-plane vibration is found at 617 and 918 cm^{-1}. Hydroxyl bending peaks of CMCD were identified at 3560 and 624 cm^{-1}. The bands attributed to absorbed water were also found at 870 cm^{-1}.

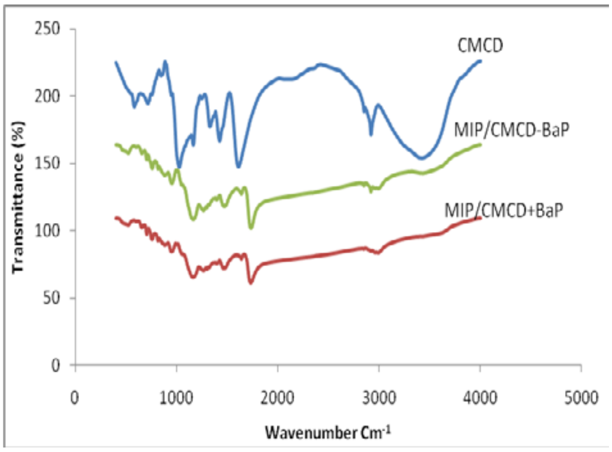
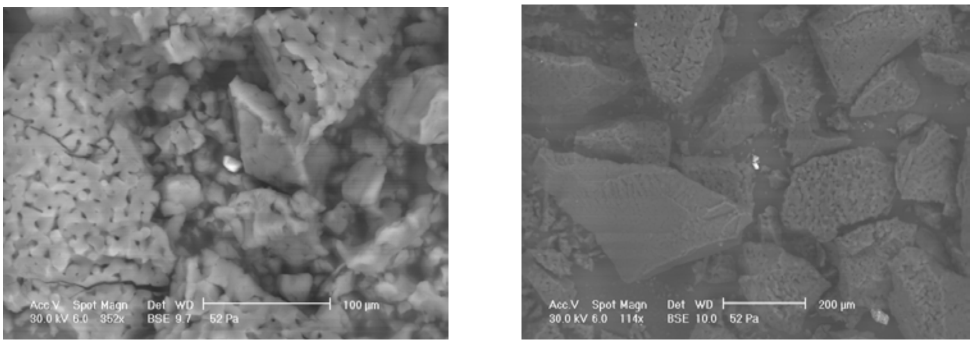


Fig. 2: FTIR curves of the prepared materials

Formation of specific cavities into polymer matrix plays an important role in the selective reorganization of B(a)P in adsorption tests. The surface morphology of both free and loaded polymer were examined using scanning electron microscopy. Irregular shapes were found in samples as shown in Fig.(3). Images of prepared MIPs show that the prepared molecular imprinting material has abundant pores on the coarse surface. It is obvious that the morphology of MIP/CMCD-BaP strongly affects the recognition and adsorption of small molecules. The free imprinted polymer (MIP/CMCD-BaP) was observed to have rougher surface than the loaded one (MIP/CMCD + BaP) which can be attributed to the filling of cavities by B(a)P during the adsorption process.



MIP/CMCD+BaP **MIP/CMCD-BaP**

Fig. 3: Sem morphology of polymer with and without BaP

Taguchi design analysis:

Taguchi results:

Taguchi orthogonal array L9 (3^3) shows the effect of pH, dose and concentration on the adsorption process of the benzo(a)pyrene on to imprinted polymer. The more the S/N ratio the more the condition favourable for adsorption. In the present work, the-higher-the-better S/N ratio was selected as the category of quality characteristic, in Fig(4). According to the outputs, increasing pH, dose and concentration increased the SNR response. Effectively optimizing all the influencing factors is of critical importance for maximizing the BaP adsorption. In this study, “larger is better” response category was adopted for optimizing the parameters as mentioned above. Thus, the SNR values are purposed to be large. A high value of the SNR infers that the signal is much higher than the random effect of the noise factors. The parameters having the highest SNR grant the optimal performance with minimum variance. These optimal parameters were pH (A) 9, adsorbent dosage (B) of 5 g with concentration (C) of 5 mg/l.

Main effect plot:

Fig (5) displays a matrix plot for three factors. This graph shows a full interactions plot matrix. The plot is used to visualize the relationship between the variables and output response. The benzo(a)pyrene adsorption efficiency increased when the pH increased from 2 to 9 with the excess of polymer enhanced the amount of non-specific rebinding for BaP removal Fig(5). The results demonstrate that the BaP removal was mainly dependent on the possible π-π interactions between the imprinted polymer and BaP molecules, in addition, the cavity of the CD has a fixed size and only the compounds with suitable molecular size and appropriate structure can be trapped in the cavity, leading to certain selectivity toward host molecules. Considering the size of BaP (0.71 nm), b-CD with the width of 0.75 nm is suitable for dimensional matching of BaP (Schneider, H.J., *et al*., 1998). Due to the hydrophobic nature of BaP template and hydrophobic core of β-CD, the BaP template should be inserted into the cavity of the β-CD residues. The H NMR analysis was conducted to investigate the formation of the inclusion complex between styrene-CMCD and BaP. In the present study, the high adsorption of BaP onto IMP is due to the well-defined pores with specific binding energy (*π-π* interactions). The reason for efficient adsorption of BaP could be (i) presence of high energy, well defined adsorption cavities in the polymer and (ii) the planarity of BaP. The adsorption capacity was increased with an increase in BaP concentration. If BaP compounds present an appropriate molecular size and structure to enter into the CD cavity the more hydrophobic the organic substances, the more stable the inclusion complexes. This finding can be explained by the fact that generally MIPs can recognize their template molecules via the existence of memory cavities with fixed size, shape, binding sites, and specific binding interaction between the target molecule and sites. It is observed from the table that the highest BaP removal of 64.66 %, 63.3 % and 63% for the pH, dose and concentration, respectively.

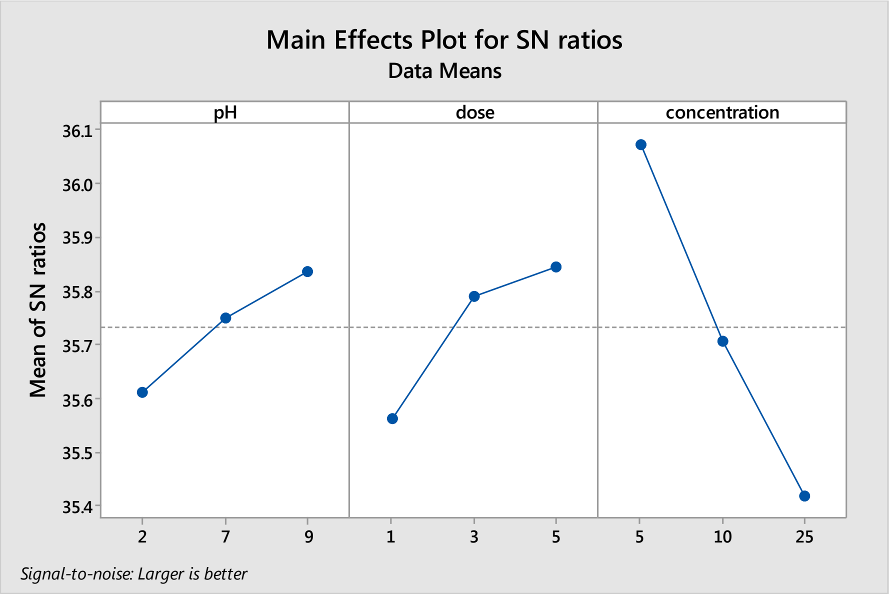


Fig. 4: Response table for mean S/N ratios for BaP–MIP-CMCD adsorption

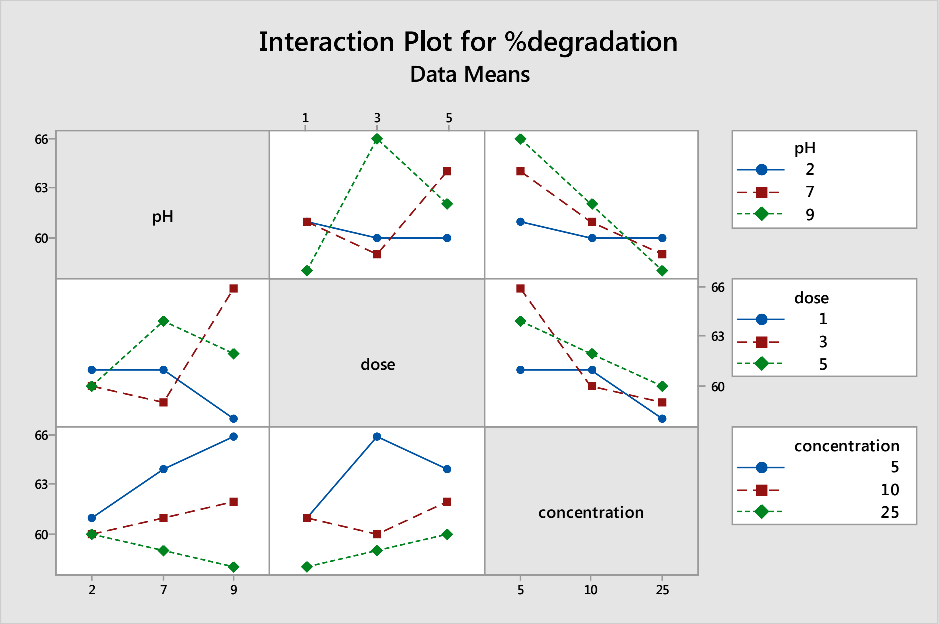


Fig. 5: interaction plot for BaP–MIP-CMCD adsorption

Implementation of ANOVA:

In order to conduct an analysis of the relative importance of each factor more systematically, an ANOVA was applied to the data. The main objective of ANOVA is to extract from the results how much variations each factor causes relative to the total variation observed in the result (Baklanov, A., *et al.*, 2007). The results of ANOVA are listed in Table (3), degree of freedom for the error is 2. According to the results, the F-ratio (0.76) for pH is smaller than the the F-Ratio for dose (1.24) and concentration (5.92). This means that the variance in pH is insignificant compared with the variance in dose and concentration that has a significant effect on the responses, it is observed form the table the most influential factor was because P value is 0.145 then the less significant variable is dose and pH. Quantitative evaluation can be achieved using percentage contribution (P%) (Latimer, J., J. Zheng, 2003). Percent contributions of all factors are presented in Table (3). The order of importance of factors is as follows: Concentration > dose > pH.

Table 3: ANNOVA Table

Source	Degree of freedome	Sum of squares	Mean of squares	F-value	P-value	Percentage contribution =ss/ss(tota)*100
pH	2	4.222	2.111	0.76	0.568	8.5
Dose	2	6.889	3.444	1.24	0.446	13.9
Concentration	2	32.889	16.444	5.92	0.145	66.36
Error	2	5.556	2.778			
Total	8	49.556				

Selectivity detection of PAHs in crude oil contaminated water:

After the investigation of the optimum conditions, these conditions were used to implement the selectivity of different PAHs as Naphthalene (Naph), Acenaphthalene (Ace), Phenanthrene (Phen), Benzo(b)fluoranthene (BpF), Benzo(a)Pyrene (BaP), and Indeno(1,2,3-c,d)Pyrene (IP) in crude oil contaminated water. About 20 ml of water was spiked with PAHs to make a final concentration of 5 mg/l and extracted using MIP/CMCD-BaP. The % removal was determined as shown in Fig (6). The MIP/CMCD-BaP showed high recoveries for Naph, Phen and BbF between 96%, 100% and 100% respectively and low recoveries for Ace, BaP and IP which were between 14.7%, 48.3% and 33% respectively. This could be ascribed to the presence of imprinted cavities in MIP/CMCD-BaP resulted in high adsorption capacity due to specific recognition. The widths of naphthalene, fluorene, phenanthrene, and pyrene range from 0.74 to 0.90 nm, which seem to be mandatory to fit into the cavity-like structure. On the other hand, the inclusion of (IP) into the cavity-like structure may be prohibited due to its bulky shape and, consequently, it would be retained to a lesser extent than their planar analogues.

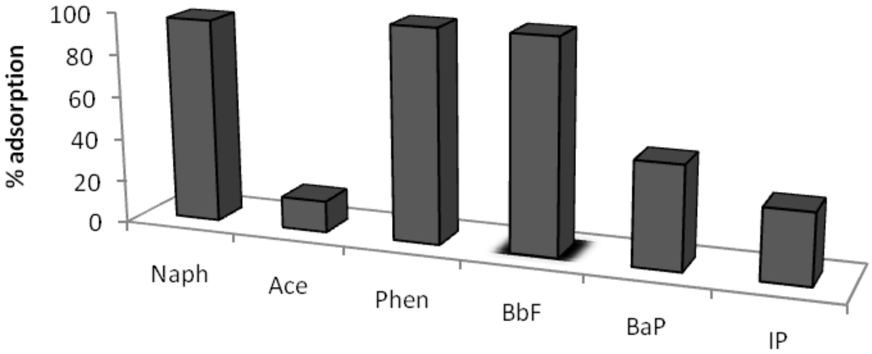


Fig. 6: % Selective adsorption of different PAHs

REFERENCES

Akiyama, T., T. Hishiya, H. Asanuma, M. Komiyama, 2001. Molecular imprinting of cyclodextrin on silica-gel support for the stationary phase of high-performance-liquid-chromatography. *J. Incl. Phenom.*, 41: 149-153.

Antwi-Boampong, S., K.S. Mani, J. Carlan, J.J. BelBruno, 2014. A selective molecularly imprinted polymer-carbon nanotube sensor for cotinine sensing. *J. Mol. Recognit.*, 27: 57-63.

Asanuma, H., T. Akiyama, K. Kajiya, T. Hishiya, M. Komiyama, 2001. Molecular imprinting of cyclodextrin in water for the recognition of nanometer-scaled guests. *Anal. Chim. Acta*, 435: 25-33.

Baklanov, A., O. Hänninen, L.H. Slørdal, J. Kukkonen, N. Bjergene, 2007. B. Fay Atmos Chem Phys, 7 : 855-874.

Chockalingam, K., N. Jawahar, K. Ramanathan and P. Banerjee, 2006. "Optimization of stereolithography process parameters for part strength using design of experiments," The International Journal of Advanced Manufacturing Technology, 29: 79-88.

Guo, T.Y., Y.Q. Xia, G.J. Hao, M.D. Song, B.H. Zhang, 2004. Biomaterials, 25: 5905.

Hillberg, A.L., K.R. Brain, C.J. Allender, 2009. Design and evaluation of thin and flexible theophylline imprinted polymer membrane materials. *J. Mol. Recognit.*, 22: 223-231.

Hishiya, T., T. Akiyama, H. Asanuma, M. Komiyama, 2002. Molecular imprinting of cyclodextrins leading to synthetic antibodies. *J. Incl. Phenom.*, 44: 365-367.

Hosoya, K., K. Yoshizako, Y. Shirasu, K. Kimata, T. Araki, N. Tanaka, *et al*. 1996. J Chromatogr A 728: 139.

Huang, J.T., S.H. Zheng, J.Q. Zhang, 2004. Polymer, 45: 4349.

Huang, X., H. Zou, X. Chen, Q. Luo, L. Kong, 2003. Molecularly imprinted monolithic stationary phases for liquid chromatographic separation of enantiomers and diastereomers. *J. Chromatogr. A*, 984: 273-282.

Kanchanamayoon, W., N. Tatrahunl, 2008. Determination of polycyclic aromatic hydrocarbons in water samples by solid phase extraction and gas chromatography. World J Chem., 3: 51-54.

Lakshmi, D., A. Bossi, M.J. Whitcombe, I. Chianella, S.A. Fowler, S. Subrahmanyam, E.V. Piletska, S.A. Piletsky, 2009. Electrochemical sensor for catechol and dopamine based on a catalytic molecularly imprinted polymer-conducting polymer hybrid recognition element. *Anal. Chem.*, 81: 3576-3584.

Latimer, J., J. Zheng, 2003. The sources, transport, and fate of PAH in the marine environment P.E.T. Douben (Ed.), PAHs: an ecotoxicological perspective, John Wiley and Sons Ltd, New York.

Logothetis, N., 1997. "Management for total quality," ed: Prentice-Hall, Upper Saddle River, NJ.

Ma, X., J. Liu, Z. Zhang, L. Wang, Z. Chen, S. Xiang, 2013. The cooperative utilization of imprinting, electro-spinning and a pore-forming agent to synthesise β-cyclodextrin polymers with enhanced recognition of naringin. *RSC Adv.*, 3: 25396-25402.

Morillo, E., M.A. Sanchez-Trujillo, J.R. Moyano, J. Villaverde, M.E. Gomez-Pantoja and J.I. Perez-Martinez, 2012. PLoS One, 7: 44137.

Piletsky, S.A., E.V. Piletskaya, A.V. Elgersma, K. Yano, I. Karube, 1995. Biosens Bioelectron, 10: 959.

Puoci, F., G. Cirillo, M. Curcio, F. Iemma, U.G. Spizzirri, N. Picci, 2007. Molecularly imprinted solid phase extraction for the selective HPLC determination of α-tocopherol in bay leaves. *Anal. Chim. Acta*, 593: 164-170.

Roy, R.K., 1990. A primer on the Taguchi method. Van Nostrand Reinhold, New York, USA, ISBN:13-9780442237295, p: 247.

Schneider, H.J., F. Hacket, V. Ru¨ diger, 1998. NMR studies of cyclodextrins and cyclodextrin complexes. Chem. Rev., 98: 1755-1786.

Shi, H.Q., W.B. Tsai, M.D. Garrison, S. Ferrari, B.D. Ratner, 1999. Nature, 398: 593.

Sreenivasan, K., 1996. Grafting of β-cyclodextrin-modified 2-hydroxyethyl methacrylate onto polyurethane.*J. Appl. Polym. Sci.*, 60: 2245-2249.

Taguchi, G. and Y. Wu, 1979. Introduction to off-line quality control: Central Japan Quality Control Assoc.

Tamayo, F.G., M.M. Titirici, A. Martin-Esteban, B. Sellergren, 2005. Anal ChimActa, 542: 38.

Tang, S., L. Kong, J. Ou, Y. Liu, X. Li, H. Zou, 2006. Application of cross-linked β-cyclodextrin polymer for adsorption of aromatic amino acids. *J. Mol. Recognit.*, 19: 39-48.

Tarbin, J.A., M. Sharman, 2001. Anal Chim Acta, 433: 71.

Wang, X.J., M.L. Brusseau, 1995. Environ.Sci.Technol., 29: 2346-2351.

Wulff, G., A. Sarhan, 1972. The use of polymers with enzymeanalogous structures for the resolution of racemates. Angew Chem Int Ed Engl, 11: 341-343.

Xu, Z., D. Kuang, L. Liu, Q. Deng, 2007. Selective adsorption of norfloxacin in aqueous media by an imprinted polymer based on hydrophobic and electrostatic interactions. *J. Pharm. Biomed. Anal.*, 45: 54-61.

Xu, Z.F., G. Wen, D.Z. Kuang, F.X. Zhang, S.P. Tang, 2013. Selective separation of deltamethrin by molecularly imprinted polymers using a β-cyclodextrin derivative as the functional monomer. *J. Environ. Sci. Health B*, 48: 336-343.