Jurnal Akta Kimia Indonesia
INDONESIA CHIMICA ACTA

PAPER

View Article Online
View Journal View Issue

Cite this: *Indo. Chim. Acta.*, 2021, **14**, 2.

Determination of Kinetics and Adsorpsi Capacity of Molecularly Imprinted Polymers Dibutylphthalate As Adsorbent

St Fauziah[1*], Fausan Sullahi[1], Nunuk Hariani Soekamto[1], Paulina Taba[1]

Received Date:
3rd November 2021
Accepted Date:
30th December 2021

Keywords:
kinetic;
adsorption;
MIP;
phthalate,
DBP

DOI:
http://dx.doi.org/10.20956/ica.v14i3.18588

Abstract. Molecularly Imprinted Polymers (MIP) are polymers with active sites that can recognize target molecules selectively. This research aims to determine the kinetics and adsorption capacity of MIP_DBP. The polymers was synthetized using methacrylic acid (MAA) monomer, Ethyleneglycol Dimethacrylate (EGDMA) cross linker, DBP as a template molecule, and toluene as a solvent. MIP_DBP was synthesized through several stages, namely: pre-polymerization, polymerization, and extraction. Then the MIP_DBP is characterized using SEM. The MIP_DBP obtained is a white solid with an average grain diameter of 1 μm and a relatively uniform size with a bead-like shape. The results of the MIP_DBP adsorption kinetics test followed the pseudo-second-order kinetics model and the adsorption capacity according to the Freundlich isothermal adsorption model with the adsorption capacity value for DBP was 9.38 mg/g.

Introduction

The use of plastic as food and beverage packaging cannot be avoided in everyday life. Plastic is a synthetic polymer material that is cheap and easy to obtain and very practical in its use. However, in the plastic production process, various additives such as plasticizers are added to obtain the desired plastic characters such as clear, strong, wide and flexible temperature tolerance range (Ilmiawati et al., 2017). The manufacture of plastics is carried out by polymerization, namely by connecting several parts of the molecular unit or monomer. For example, plastic type PVC (Polyvinyl Chloride) is composed of vinyl chloride monomer.

In addition to the main ingredients called monomers, there are non-plastic materials called additives. Additives can be in the form of low molecular substances such as anti-adhesive, antioxiandts, plasticizers and many more. (Koswara, 2006; Pipit, 2008).

Phthalate compounds and their derivatives such as dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), di-2-ethylhexyl phthalate (DEHP), and diisononyl phthalate (DINP) are used as plasticizers which are widely added in plastic base materials (Ilmiawati et al., 2017).

Dibutylphthalate (DBP) is often used in the manufacture of plastics, to increase their flexibility and plasticity, such as beverage bottles and food wrappers. DBP is a fat-soluble component, because it can enter the body through contamination of food and drinks packaged in plastic containers. DBP compounds are organic compounds that are carcinogenic. Therefore, it is necessary to analyze the levels of DBP compounds in food and beverages packaged in plastic. One of the preparation methods that is often carried out before a compound in food and beverage samples is analyzed is solid phase extraction (SPE) method (Zhang et al., 2013), because it has a simple, low cost and more selective (Kishore Kumar Jagadeesan, et.al, 2017). The selection of the right adsorbent to be important factor in SPE extraction method. MIP are the right adsorbent choice in the SPE method (Yang et al., 2014).

Imprinted polymer is a technique of placing the active site of the target molecule on the MIP in order to selectively recognize the target molecule. Therefore MIP is known as a smart material (Surikumaran et al., 2014). The advantages

[1]*Department of Chemistry, Faculty of Mathematics and Sciences, Hasanuddin University, 90245, Makassar, Indonesia;* ***Email:*** **stfauziah@unhas.ac.id**

of MIP are its high selectivity and affinity for target molecules, resistance to temperature and pressure increases, and low cost (Vasapollo et al., 2011).

MIP has been widely used in the extraction process, purification, and as a chemical sensor with the advantages of being more resistant to conditions and can be used for large numbers of samples (Yang et al., 2014; Vasapollo et al., 2011).

The binding test between MIP and the molecular template was carried out to create adsorption and adsorption isotherms of MIP and NIP. The adsorption capacity was determined through the adsorption otherm equation (Ferdaous Arfaoui, et.al., 2017). The adsorption kinetic parameters were determined through kinetic measurements based on pseudo-first-order and pseudo-second-order kinetic models (Nor A. S. Khairi et.al., 2015).

Based on the description of the research development of the research above, it is necessary to make MIP DBP as an adsorbent using MAA and a different cross-linker, namely EGDMA with the precipitation polymerization method where the research conducted by using trimethylolpropane trimethacrylate (TRIM) as a cross-linker by Tabarestani MS, et.al., 2016 and this is a novelty in this research.

Experimental

Material and tools

Chemicals used include MAA (Merck), EGDMA (Merck), AIBN (Merck), DBP (Merck), toluene (Merck), acetone (Merck), methanol (Merck), Acetate acid (Merck). All of the reagents were analytical grade and nitrogen gas.

The tools used include glassware, analytical balances, round bottom flasks, shakers, ovens, sonicators, pH meter, water bath, UV Vis (Shimadzu, UV-2600), and SEM (Tescan Vega 3SB).

The MIP and NIP synthesis

The pra polymerization stage, MAA monomers as much as 0.3278 ml (4 mmol) and DBP mixed as much as 0.2651 ml (1 mmol) in the round ground flask then left for a while, then an EGDMA cross binder is then added as much as 1.5087 ml (8 mmol) and the mixture is dissolved using 50 mL of porogen toluene solvents. The solution was sonicated for 10 minutes, then flowed with nitrogen for 10 minutes to eliminate oxygen. Then 5 ml (1 mmol) of AIBN as initiator was added to the solution. The solution was sonicated again for 15 minutes and then flowed with nitrogen for 15 minutes. The next step is polymerization on the water bath at 60°C for 24 hours (Dounia Elfadil, et.al., 2021).

The polymer formed was filtered and washed with acetone, methanol and distilled water respectively. Then, the DBP molecule was eliminated from the polymer using solvents of methanol: acetic acid (9:1) through a sonication process for 30 minutes. Then the MIP was dried and saved. Non Imprinted Polymers (NIP) is made in the same way without using DBP without the extraction process (Tabarestani, 2016; which et al., 2015).

Characterization of MIP_DBP

MIP is only characterized using SEM to find out the morphology of the surface of the MIP.

Determination of MIP_DBP Adsorption Kinetics

Determination of adsorption kinetics can be determined from the data analysis of the effect of time using the equation of one pseudo and the two pseudo orders (Dai et al., 2013).

Determination of MIP_DBP Adsorption Capacity

Determination of adsorption capacity can be determined from data analysis of the effect of concentration using the Isotermal Adsorption equation Freundlich and Isothermal Langmuir (Ramakrisna and Viraghavan, 1997).

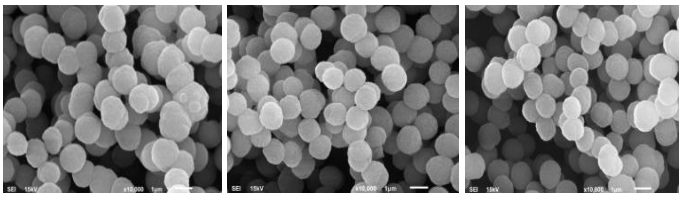
Result and Discussion

Synthesis of MIP_DBP

MIP was synthesized using MAA monomer combined with EGDMA crossfield and using DBP as a template molecule. NIP was synthesized in the same way without the use of DBP. The polymer is a white solid resembling granules of uniform shape and size.

Characterization of NIP and MIP using SEM

Characterization of Surface Morphology of NIP_MAA-Co-EGDMA, MIP_MAA-Co-EGDMA(BE) or MIP_DBP(BE) and MIP_MAA-Co-EGDMA (AE) or MIP_DBP(AE) using SEM can be seen in Figure 1. The MIP_DBP and NIP grains diameter are an average of 1 μm and a relatively uniform size with a bead-like shape.



(a) (b) (c)

Figure 1. Morphology of Surface (a) NIP_DBP_MAA-Co-EGDMA magnification 10,000x, (b) MIP_DBP(AE) magnification 10,000x, (c) MIP_DBP(BE) magnification 10,000x.

Determination of DBP Adsorption Kinetics by MIP

The data obtained from the variation of the time effect against the DBP adsorption ability by MIP was shown in Table 1. The results of the analysis of the effect of time on

the adsorption ability of DBP by MIP are shown in Table 1.

Table 1. Data of time effect against the number of DBP associated by MIP_DBP_MAA-Co-EGDMA(AE).

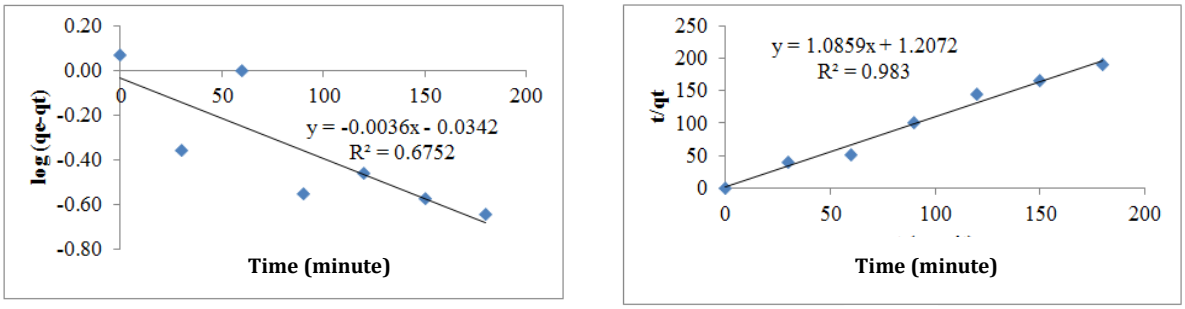
No.	Sample	Time (minute)	C_e (mgL^{-1})	q_e (mg/g)
1	MIP_DBP	30	5.592	0.7346
2	MIP_DBP	60	2.952	**1.1746**
3	MIP_DBP	90	6.472	0.8946
4	MIP_DBP	120	5.032	0.8280
5	MIP_DBP	150	4.552	0.9080
6	MIP_DBP	180	5.672	0.9480

Time is an important variable in the quality of MIP as an adsorbent. The amount of DBP adsorbed by MIP increased with increasing contact time until it reached maximum adsorption at 60oC. When maximum adsorption was reached, MIP was saturated by DBP. The addition of the next time causes the adsorption ability to begin to decrease or tend to remain. Therefore, the effect of time needs to be analyzed using pseudo-first-order and pseudo-second-order equations to determine the adsorption kinetics model of MIP. Figure 2 shows the log curve (qe-qt) vs. t or curve t / qt vs t for DBP adsorption by MIP_DBP(AE) in a row is a kinetics curve of one pseudo and two orders. R2, K1 (kinetics constant of the pseudo-first-order), K2 (kinetics constant of pseudo-second-order), qe values of the calculations results and experimental results are shown in Table 2.

Table 2. Parameter data of DBP adsorption kinetics by MIP_DBP(AE) according to pseudo-first-order and pseudo-second-order kinetic equations.

MIP type	q_e			K_1	K_2	R^2	
	Pseudo-first-order	Pseudo-second-order	Experiment			Pseudo-first-order	Pseudo-second-order
MIP_DBP_MAA-co-EDMA(AE)	0.454	0.920	1.174	-0.008	1.142	0.657	0.983

Based on the data shown in Table 2, that the pseudo-second-order adsorption kinetics model all in accorandce with the synthesis MIP in this study with the net value of the adsorption rate (K2) MIP_DBP(AE) is 1.1428 g/minute.mg. Another research on the time effect to determine the adsorption rate of MIP_DBP as a comparison based on an adsorption kinetics model that follows a pseudo-first-order or pseudo-second-order model has never been done.



(a) (b)

Figure 2. (a) The Kinetics Curve of the One Pusat and (b) Kinetics curve of two pseudo orders for DBP adsorption by MIP_DBP (AE)

Determination of MIP adsorption capacity against DBP

The mechanism of DBP adsorption over active site of MIP_DBP could be illustarated on figure 3. The scheme of the adsorption mechanism begins with the MIP synthesis process using DBP as a template molecule, then the release of DBP from MIP so that it leaves the active site in the MIP cavity. Furthermore, MIP was applied as a DBP adsorbent through the mechanism of binding DBP functional groups to the active site of MIP.

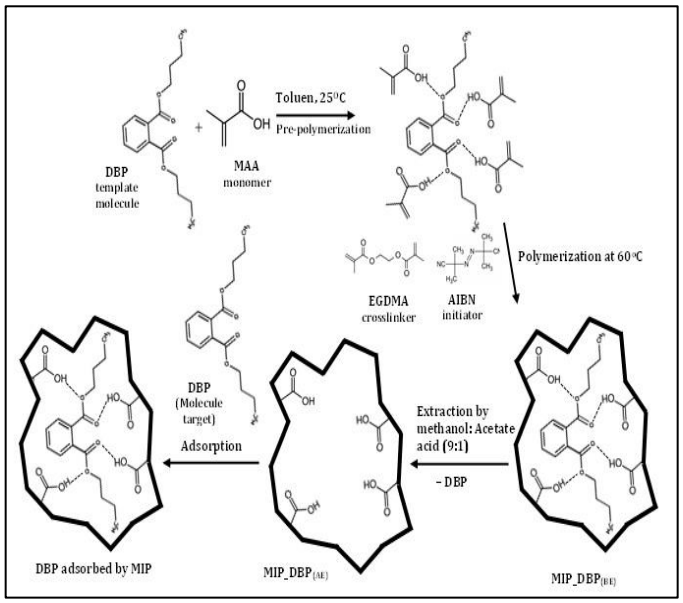


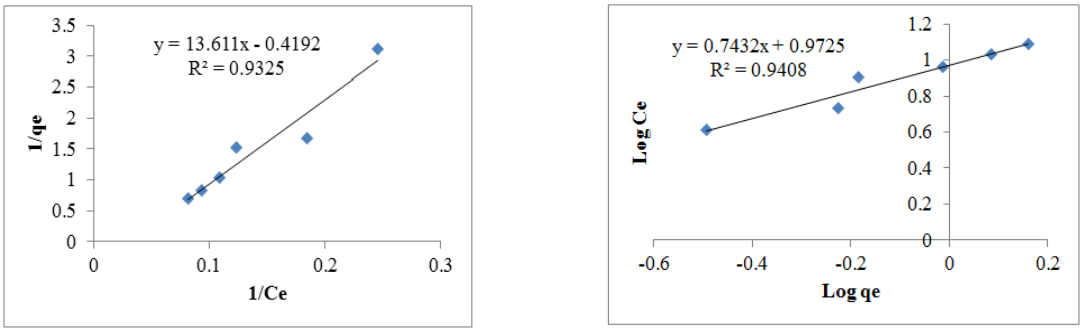
Figure 3. Mechanism synthesis MIP_DBP and adsorption DBP by MIP_DBP.

Data on the effect of concentration on the adsorption ability of DBP is shown on Table 3.

Table 3. The concentration effect data of the adsorption ability of MIP_DBP(AE) on DBP.

No.	Sample	Initial concentration C_e (mgL^{-1}) (mgL^{-1})	C_e (mgL^{-1})	q_e (mg/g)
1	MIP_DBP(AE)	6	4.072	0.3213
2	MIP_DBP(AE)	9	5.432	0.594
3	MIP_DBP(AE)	12	8.072	0.6546
4	MIP_DBP(AE)	15	9.192	0.968
5	MIP_DBP(AE)	18	10.712	1.2146

Table 3 shows that the higher the initial concentration of the DBP standard solution, the more DBP that can be adsorbed by MIP. Table 3 shows that the higher the initial concentration of DBP standard solution, the more DBP that can be adsorbed by MIP because of the large pore surface area. However, if the adsorption equilibrium has been reached, the adsorption ability of MIP tends to remain even though the concentration is increased. Figure 4 shows the Langmuir isothermal and Freundlich isothermal curves of MIP_DBP(AE), where the correlation coefficient (R2) of the two curves determines the isothermal model corresponding to MIP_DBP(AE).



(a) (b)

Figure 4. (a) Langmuir isothermal curve and (b) Freundlich isothermal curve of DBP adsorption by MIP_DBP.

Figure 4 shows that the R2 value of the Langmuir adsorption isothermal curve of MIP_DBP(AE) was 0.9325, the R2 value of the Freundlich adsorption isothermal curve obtained was 0.9408. Therefore, the Freundlich adsorption isothermal model is more suitable to be used in determining the adsorption capacity of MIP_DBP(AE). The parameter data for DBP adsorption by MIP on Table 4 based on the Langmuir and Freundlich isothermal adsorption model.

Table 4. Parameters of DBP adsorption by MIP_DBP_MAA(AE) obtained based on the equations of Langmuir adsorption isothermal and Freundlich adsorption isothermal.

MIP type	Langmuit adsorption isotermal			Freundlic adsorption isotermal		
	b	Q_0	R^2	Kf	n	R^2
MIP_DBP(AE)	-2.3854	0.0734	0.9325	9.38	1.3455	0.9408

On the Table 4 shows that the value of the Freundlich constant (Kf) describes the adsorption capacity by MIP_DBP(AE) was 9.38 mg/g and it's better than MIP DBP made by Junfeng Zhu, et.al., 2012. Which is 8.940mg/g. The n constant value of the MIP_DBP(AE) was 1.3455. The value of the constant n where the value of n is between 1-10 indicates that there is an effective absorption (Febrianto et al, 2009). This is indicates that the DBP adsorption process by MIP is quite effective.

Conclusion

The conclusion from this research is that functional polymers such as MIP_DBP and NIP_DBP were synthesized by precipitation polymerization technique. The surface morphology of MIP shows the presence of grains of similar size and density between grains, and the surface looks rough and stiff. The adsorption kinetics model suitable for MIP_DBP were pseudo-second-order adsorption kinetics model with the correlation coefficient (R2) is 0.983 and the adsorption rate constant (K2) is 1.1428 g.min-1.mg-1. The adsorption capacity of MIP_DBP was in accorandce with the Freundlich isothermal adsorption model with the adsorption capacity value of 9.38 mg/g. MIP_DBP can be used as selective adsorbent in the SPE method for cleanup and preconcentration.

Conflict of Interest

The authors declare that there is no conflict of interest.

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