Synthesis and Characterization of a Molecularly Imprinted Polymer for 2,4-Dinitrophenol Uptake Using 4-Vinylbenzoic Acid as the Complexing Monomer

Nor Dyana Zakaria, Nor Azah Yusof[*], Md Jelas Haron and Abdul Halim Abdullah

Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

*Corresponding author: Fax: +3 89435380; Tel: +3 89466782; E-mail: azah@science.upm.edu.my

A new technique for analysis of 2,4-dinitrophenol in water at low concentration is proposed based on a molecular imprinted polymer. Molecular imprinted polymer (MIP) is cross linked polymeric materials that exhibit high binding capacity and selectivity towards target molecules (template) purposely present during the synthesis process. The molecular imprinted polymer was prepared in bulk, radical polymerization method using 2,4-dinitrophenol, 4-vinylbenzoic acid, ethylene glycol dimethacrylate and benzoyl peroxide as template, functional monomer, cross-linker and initiator, respectively. Adsorption process for removal of nitrophenol by molecular imprinted polymer was evaluated under various conditions to determine the effect of pH, adsorption kinetics, the isotherm and its selectivity. The maximum adsorption of 2,4-dinitrophenol was 2.50 mg/g. The adsorption of 2,4-dinitrophenol by 4-vinylbenzoic acid was found most effective at pH 5.0. Kinetics study showed that 2,4-dinitrophenol adsorption was modeled by second order kinetic. Adsorption isotherm data could be interpreted using the Langmuir equation.

Key Words: Molecular imprinted polymer, 2,4-Dinitrophenol.

INTRODUCTION

The determination of phenol derivatives is very important in food, medical, environmental ground and surface water. Some of them may cause the danger to the health and environmental pollution because of their inherent toxicity. Nitrophenol are of interest, as they are listed as priority toxics pollutants by the United States Environmental Protection Agency. A phenol concentration of 1 mg/L or greater, affects aquatic life and can cause major risks to human health. Therefore, in most cases, stringent effluent discharge limit of less than 0.5 mg/L are imposed. In this sense, the US EPA has established a limit concentration of 1 µg/L for phenolic compounds for drinking water[1]. Methods that have been developed for the removal of nitrophenols from water include microbial degradation and chemical oxidation. Slow reaction rates, disposal of sludge and control of temperature and pH are all drawbacks associated with microbial degradation[2] while chemical oxidation is only economically feasible at high concentrations[3]. Many methods are available for removal of phenolic compound, such as an electro-assisted process employing a modified electrode[4,5], using chemical sorbents[6] such as Amberlite® XAD-4, a hypercross linked polymeric compound[7,8] and biosorbents[9,10]. Among the many available methods for removal of phenolic compounds, molecular imprinted polymer is one that offers excellent selectivity towards the target molecules. The good

selectivity obtained with molecular imprinted polymer-based separation materials has led them being considered as promising selective sorbents for solid phase extraction (SPE). As an extension this method is now being extensively investigated as highly selective solid phase extraction sorbents for washing and the preconcentration of samples prior to analysis[11].

Molecular imprinted polymer is a method for making selective template binding sites in synthetic polymers by using molecular template. Target molecules (*i.e.*, phenolics) can be used as templates for imprinting cross-linked polymers. After the removal of template, the remaining polymer is more selective. The selectivity of the polymer depends on various factors such as the size and shape of the cavity and rebinding interactions. Covalent interactions, non-covalent interactions such as hydrogen bonding, π-π bonding and hydrophobic interaction, electrostatic interactions and metal ion coordination can be exploited to organize the functional monomers around the template[12].

In this work, the precipitation polymerization was employed to prepare molecular imprinted polymer for 2,4-dinitrophenol in acetonitrile using phenolic compounds, acrylamide, ethylene glycol dimethacrylate (EGDMA) and benzoyl peroxide (BPO) as template, functional monomer, cross-linker and initiator, respectively. The characteristics of

the obtained polymers were analyzed through Fourier transformed infrared (FTIR) spectroscopy and particle size analyzer (PSA). The parameter studies include effect of pH, adsorption kinetics, adsorption isotherm and its selectivity. The selectivity of the obtained particles was elucidated by studying the different rebinding capabilities of 2,4-dinitrophenol samples and structurally related compounds.

EXPERIMENTAL

4-Vinylbenzoic acid, 2,4-dinitrophenol, ethylene glycol dimethacrylate (EGDMA) and benzoyl peroxide (BPO) were obtained from Fluka (Switzerland). All other chemicals were of reagent grade and purchased from Merck (Germany).

Preparation of dinitrophenol-imprinted polymer: For the preparation of the molecular imprinted polymer using the non-covalent approach based on hydrogen bonding interaction, the template 2,4-dinitrophenol (1.84 g, 1.0 mmol) was dissolved in acetonitrile (30 mL). The functional monomer, 4-vinylbenzoic acid (0.7408 g, 5.0 mmol), the cross-linking, ethylene glycol dimethacrylate (EDGMA) (2.93 g, 15 mmol) and the initiator, benzoyl peroxide (BPO) (3.87 g, 1.6 mmol) were then added. After degassing and nitrogen purging for 10 min, the flask was sealed and the material was allowed to polymerize at 70 °C for 24 h in a water bath. The obtained bulk polymers were crushed, ground and sieved to obtain regularly sized particles between 80-100 μm. The polymer particles were extracted with methanol:acetic acid (1 %) (2:1) (30 mL) for three times to remove the 2,4-dinitrophenol template molecule. The particles were then extensively washed with water until no more 2,4-dinitrophenol was released. The concentration of 2,4-dinitrophenol was analyzed with UV-vis spectrometer. Non-imprinted polymer (NIP) was prepared and treated with the same method in the absence of 2,4-dinitrophenol.

Adsorption studies: Adsorption of 2,4-dinitrophenol from aqueous solutions was investigated in batch experiments in triplicates. The effects of pH, adsorption isotherm, kinetics and selectivity were studied. 0.05 g of molecular imprinted polymer was shaken for 1 h in 20 mL of 10 ppm 2,4-dinitrophenol. The pH was adjusted with hydrochloric acid (HCl) or sodium hydroxide (NaOH). The concentration of 2,4-dinitrophenol in the aqueous after desired treatment periods was analyzed by using UV-Vis spectrometer. The adsorption capacity was calculated as below:

$$\text{Adsorption capacity (q)} = \frac{(C_0 - C_e) \times V}{M} \qquad (1)$$

where q (mg/g) = total adsorption of 2,4-dinitrophenol, C_0 and C_e = initial and equilibrium concentrations of 2,4-dinitrophenol in solution (mg/L), respectively. V (L) = solution volume and M (g) = molecular imprinted polymer weight. Adsorption kinetics were studied by shaking molecular imprinted polymer (0.05 g) in 20 mL of 2,4-dinitrophenol (10 ppm) for various time periods (5, 10, 20, 30, 60, 120, 240, 480, 960 and 1440 min) at pH optimum for 10 mg/L. The adsorption isotherm was studied by 0.05 g of molecular imprinted polymer shaken in 20 mL of 2,4-dinitrophenol solution with different concentration (1, 2, 4, 8, 10, 15, 20 and 30 mg/L) at optimum pH for 1 h.

Selectivity of the fabricated molecular imprinted polymer towards phenol, 3-chlorophenol and 2,4-dichlorophenol with respect to 2,4-nitrophenol was studied. A solution (25 mL) containing 10 mg/L (for each compound) was mixed together and treated with molecular imprinted polymer (0.05 g) at room temperature. The concentration of the phenolic compounds after treatment was measured by UV-vis spectrometer. The binding capacity and the distribution coefficient were calculated.

Characterization of molecular imprinted polymer: Characterizations of the imprinted polymer were carried out using Fourier transformed infrared (FTIR). The imprinted polymer particles (*ca.* 0.01 g) were thoroughly mixed with KBr and pressed into a pellet and FTIR spectrum was recorded from 4000-450 cm^{-1}.

RESULTS AND DISCUSSION

FTIR spectra of 2,4-dinitrophenol imprinted polymer and monomer: The IR spectra of the 2,4-dinitrophenol imprinted polymer and monomer materials were recorded using the KBr pellet method. The spectral differences between molecular imprinted polymer and monomer 4-vinylbenzoic acid are shown in Fig. 1. Both spectra indicated the presence of CO carbonyl groups at 1718 and 1705 cm^{-1}. The interaction between template and monomer gave a shift in peaks in the molecular imprinted polymer spectrum, which showed a broad OH stretching peak at 3444 cm^{-1} and CH stretching at 2957 cm^{-1}, while the CH stretching in the spectrum of monomer was at 2977 cm^{-1}.
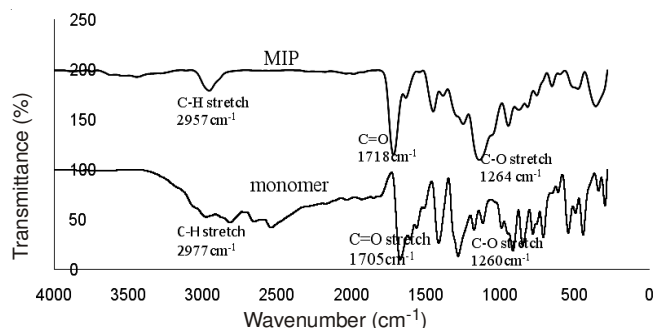

Fig. 1. IR spectra for molecular imprinted polymer and monomer

Effect of pH study: External solution pH was found to be an important variable affecting the adsorption process. The effects of pH on the adsorption of 2,4-dinitrophenol on molecular imprinted polymer are shown in Fig. 2. The adsorption was measured at pH range 1-10. The maximum adsorption capacity of 2,4-dinitrophenol was found to be 2.59 mg/g under acidic condition at pH 5.0. Higher sorption of 2,4-dinitrophenol onto molecular imprinted polymer relative to non-imprinted polymer could be attributed to the stronger interactions between molecular imprinted polymer and 2,4-dinitrophenol or nitrophenolate ion. 2,4-Dinitrophenol is a polar molecule due to the nitro group and has a pK$_a$ of 7.15. The interaction between adsorbent molecular imprinted polymer and the adsorbate is a cation-dipole interaction as well as van der Waals forces in acidic solutions. Furthermore H-bonding is possible between the hydroxyl group of 2,4-dinitrophenol
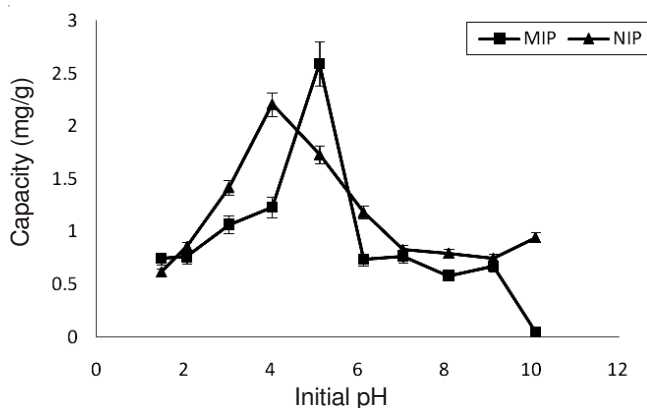
Fig. 2. Effect of pH on removal of 2,4-dinitrophenol by molecular imprinted polymer

and the carbonyl groups of the adsorbent in acidic solutions. On the other hand, mainly a cation-anion attraction or anion exchange process between molecular imprinted polymer and the nitrophenolate ion involves in the sorption in basic solutions.

Effect of kinetic study: The rate of 2,4-dinitrophenol adsorption by molecular imprinted polymer was measured as a function of time. The result for kinetic study for 2,4-dinitrophenol adsorption is shown in Fig. 3. The sorption process of 2,4-dinitrophenol was rapid at the initial stage and rather slow when approaching equilibrium. The maximum adsorption capacity occurred after 1 h at capacity around 2.50 mg/g.
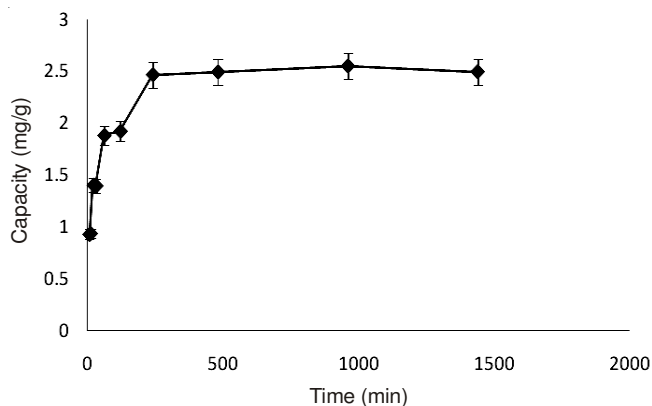

Fig. 3. Adsorption rate of 2,4-dinitrophenol by molecular imprinted polymer

Kinetic characteristic in an exchanger or a sorbent material depends not only in the presence of active site on it but also depends on the accessibility of the site without sterical hindrance which is greatly determined by the sorbent matrices. Sorption process is known to be controlled by different kinds of mechanisms such as mass transfer, chemical reactions and particle diffusion. Hence, several kinetic sorption models were applied to evaluate the experimental data. For this purpose Lagergren's pseudo-first-order kinetic model, pseudo-second-order kinetic model and intra particle diffusion model were applied.

Fig. 4 shows that the pseudo- second order model can described the sorption kinetics of 2,4-dinitrophenol. In order to explore the kinetics involved in 2,4-dinitrophenol sorption,
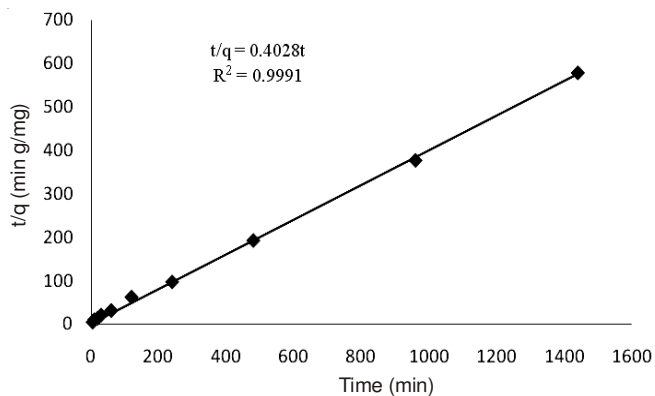

Fig. 4. Second order kinetic plot for adsorption 2,4-dinitrophenol by molecular imprinted polymer

the experimental data were fitted into the following equations:

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

where k_2 (min^{-1}) = rate constant of pseudo-second-order sorption, q_t denotes the amount of 2,4-dinitrophenol sorption (mg/g) at time, t (min) and q_e denotes the amount of 2,4-dinitrophenol adsorption (mg/g) at equilibrium.

The equilibrium removal of 2,4-dinitrophenol was mathematically expressed in terms of adsorption kinetics. The correlation coefficients, r^2 of the plots indicate that the pseudo-second-order kinetic equation (Fig. 4) provided a better model for describing the sorption of the 2,4-dinitrophenol by the molecular imprinted polymer compared to first-order equation.
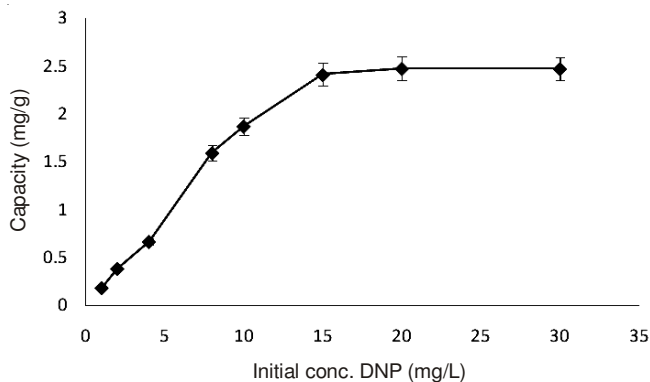

Fig. 5. Sorption capacity of various concentration of 2,4-dinitrophenol by molecular imprinted polymer

Determination of the isotherm: The sorption isotherm of molecular imprinted polymer is shown in Fig. 5. The adsorption values increased with increasing concentration of 2,4-dinitrophenol and saturated value is achieved at concentration of 15 ppm, which represents saturation of the active binding cavities on the molecular imprinted polymer.

The Langmuir isotherm is based on three assumptions: (a) adsorption cannot proceed beyond monolayer coverage, (b) all surface binding sites are equivalent and can accommodate, at most, one adsorbed template and (c) the ability of a template to bind at a given site does not depend on the

occupation of neighboring sites. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a template molecule occupies a site, no further adsorption can take place at that site. Theoretically, a saturation value is reached beyond which no further sorption can take place. Langmuir model is probably the best known and most widely applied sorption isotherm. It has produced good agreement with a wide variety of experimental data and may be represented as follows:

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \qquad (3)$$

where C_e = equilibrium concentration (mg/L), q_e = amount of 2,4-dinitrophenol sorbed at equilibrium (mg/g), q_m = amount of 2,4-dinitrophenol sorbed for a complete monolayer (mg/g) and b is a constant related to the energy or net enthalpy of sorption (L/mg). The sorption data were analyzed using the linear form eqn. 3 of the Langmuir isotherm. The plots of specific sorption, C_e/q_e, against the equilibrium concentration, C_e, for molecular imprinted polymer are shown in Fig. 6.
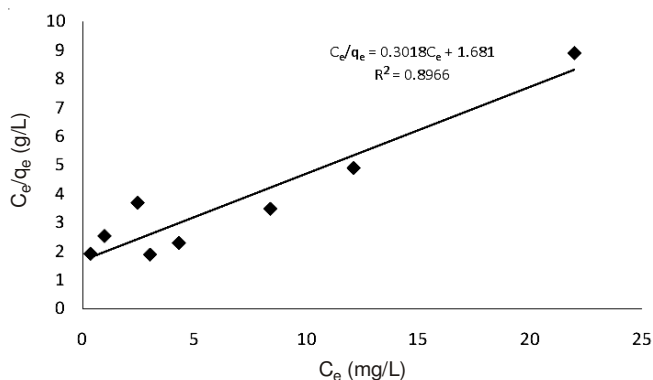

Fig. 6. Langmuir plot for solution of 2,4-dinitrophenol by molecular imprinted polymer

The Langmuir plots have a higher correlation coefficient which is 0.8966. It can be confirmed that the 2,4-dinitrophenol adsorption by molecular imprinted polymer follows the Langmuir model with the maximum sorption capacity of 2.47 mg/g at room temperature.

Selectivity study: Competitive adsorptions of phenol/2,4-dinitrophenol, 3-chlorophenol/2,4-dinitrophenol and 2,4-dichlorophenol/2,4-dinitrophenol from their mixture were conducted using imprinted and non-imprinted polymer. The effect of imprinting on selectivity was defined as

$$K_d = \frac{[C_i - C_f] \times V}{M} \qquad (4)$$

where K_d = distribution coefficient, C_i and C_f = initial and final solution concentration, respectively. V (mL) = volume of the solution and M (g) = weight of molecular imprinted polymer.

The selectivity coefficient for the binding of phenol compound in the presence of competitor species can be obtained from equilibrium binding data according to:

$$K_d = \frac{K_d \, (2,4\text{-dinitrophenol})}{K_d \,(\text{phenolic})} \qquad (5)$$

where k = selectivity coefficient and (phenolic) represents the compounds phenol, 3-chlorophenol and 2,4-dichlorophenol. A comparison of k values of the imprinted polymers with those phenolic compounds allows an estimate of the effect of imprinting on selectivity. A relative selectivity coefficient k' can be defined as:

$$k' = \frac{k_{Imprinted}}{k_{Control}} \qquad (6)$$

The binding capacity adsorption of molecular imprinted polymer for 2,4-dinitrophenol is higher than non-imprinted polymer because the molecular imprinted polymer have selective template for 2,4-dinitrophenol compared to non-imprinted polymer. Table-1 summaries K_d, k and k' values for phenol, 3-chlorophenol and 2,4-dichlorophenol with respect to 2,4-dinitrophenol. The k' values for phenol/2,4-dinitrophenol, 3-chlorophenol/2,4-dinitrophenol and 2,4-dichlorophenol/2,4-dinitrophenol are 1.68, 1.15 and 2.21, respectively. This means that 2,4-dinitrophenol can be determined using the molecular imprinted polymer even in presence of phenol, 3-chlorophenol and 2,4-dichlorophenol interferences (Fig. 7). This is due to the selectivity of the molecular imprinted polymer to the template which is 2,4-dinitrophenol.

TABLE-1
PARAMETERS INVOLVED IN SELECTIVITY STUDY
OF THE MIP AND NIP TOWARDS DIFFERENT
KIND OF PHENOLIC COMPOUND

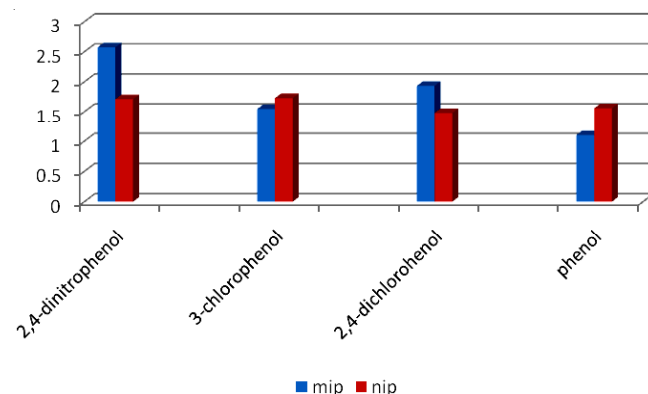|	$K_{d(MIP)}$ (mg/g)	$K_{d(NIP)}$ (mg/g)	$k_{(MIP)}$	$k_{(NIP)}$	k'
2,4-Dinitrophenol	2.57	1.71	–	–	–
Phenol	1.54	1.72	1.66	0.99	1.68
3-Chlorophenol	1.93	1.48	1.33	1.15	1.15
2,4-Dichlorophenol	1.10	1.56	2.33	1.09	2.21

Fig. 7. Selectivity study of 2,4-dinitrophenol by molecular imprinted polymer in the presence of various phenolic compound

Conclusion

The potential use of molecular imprinted polymer, prepared from 4-vinylbenzoic acid as functional monomer was investigated for the removal of 2,4-dinitrophenol from aqueous solution effectively. Adsorption of 2,4-dinitrophenol by molecular imprinted polymer- was found effective at pH 5.0. Kinetics study, showed that the rate of adsorption of 2,4-dinitrophenol

increased rapidly at the initial stage and then reduced until it reached equilibrium. Compared to Lagergren pseudo first order model, second order kinetic equation is better fit for sorption kinetic data. The adsorption increased with increasing initial concentration. The results showed that the adsorption process obeys the Langmuir adsorption isotherm.

The selectivity experiments showed that the molecular imprinted polymer is selective towards 2,4-dinitrophenol in the presence of 2,4-dichlorophenol, 3-chlorophenol and phenol interferences. This suggests that the selectivity was mainly based on the affinity of shape match to the cavity by template printing.

Molecular imprinted polymer has been successfully used as sorbents for removal and selectivity of 2,4-dinitrophenol in aqueous solution. In addition, molecular imprinted polymer is inexpensive and easy to prepare.

ACKNOWLEDGEMENTS

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