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Research Article

Preconcentration and Fluorimetric Determination of 2-Phenylphenol using Magnetic Molecularly Imprinted Polymer

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Abstract

In the present work, reusable magnetic molecularly imprinted polymers have been used for the first time as an adsorbent for the determination of 2-phenylphenol. Magnetic molecularly imprinted polymers have been used for the selective separation and preconcentration of 2-phenylphenol and native fluorescence has been used for the sensitive determination of the analyte. The developed method is rapid and determination of 2-phenylphenol was completed in 40 minutes. Limit of detection (LOD) of the method was found to be 1.09 µg L-1 and the imprinting factor was found to be 1.87. Capacities of the imprinted and non-imprinted polymers were calculated as 0.0494 µmol g−1 and 0.0265 µmol g−1 which indicates the creation of the specific binding sites on the surface of the imprinted polymer. The linearity of the calibration graph was observed within the range of 5 - 250 µg L-1. Selectivity parameters showed that the specific binding sites were available on the imprinted polymer which was capable of recognizing 2-phenylphenol molecules with their functional groups, size and shape. Scatchard analysis revealed the heterogeneous distribution of binding sites for imprinted polymer and homogeneous binding site for non-imprinted polymer. Quantitative re-binding (99.0±0.7) and recovery (98.8±0.8) values were obtained when the same imprinted polymer was used for ten times. The interference effects of some organic compounds and characterization studies were also evaluated. Relative standard deviations of intra-day and inter-day studies were found to be in the range of 1.1 - 1.5 % and 1.1 - 1.8 %, respectively. The method is applied to tap water samples and the recoveries were found to be in the range of 95.3 and 99.7 %.

Keywords: 2-phenylphenol, magnetic molecularly imprinted polymer, fluorimetric determination, preconcentration.

Manyetik Moleküler Baskılanmış Polimer Kullanımına Dayalı 2-Fenilfenol Önderiştirilmesi ve Florimetrik Tayini

Öz

Bu çalışmada, 2-fenilfenol tayini için tekrar kullanılabilir manyetik moleküler baskılanmış polimerler ilk kez bir adsorban olarak kullanılmıştır. 2-fenilfenolün seçici olarak ayrılması ve zenginleştirilmesi için manyetik moleküler baskılanmış polimerler kullanılmış ve hassas tayini için analitin doğal floresansı ölçülmüştür. Geliştirilen yöntem hızlıdır ve 2-fenilfenol tayini 40 dakikada tamamlanmıştır. Yöntemin belirtme alt sınırı (LOD) 1.09 µg L-1, baskılanma faktörü ise 1.87 olarak bulunmuştur. Baskılanmış ve baskılanmamış polimerlerin kapasiteleri sırasıyla 0,0494 µmol g-1 ve 0,0265 µmol g-1 olarak hesaplanması, baskılanmış polimerin yüzeyinde spesifik bağlanma bölgelerinin oluşturulduğunu göstermektedir. Kalibrasyon grafiğinin doğrusal aralığı 5 - 250 µg L-1 olarak bulunmuştur. Seçimlilik parametreleri incelendiğinde, moleküler baskılanmış polimer üzerinde 2-fenilfenol moleküllerini tanıyabilen fonksiyonel grup, boyut ve şekil cinsinden spesifik bağlanma bölgelerinin mevcut olduğu sonucuna varılmıştır. Scatchard analizi, moleküler baskılanmış polimer için bağlanma bölgelerinin heterojen, baskılanmamış polimer için ise homojen olduğunu ortaya

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çıkarmıştır. Aynı polimerin en az on kere kullanıldığı durumda bile nicel geri-bağlanma (99.0±0.7) ve geri-kazanım (98.8±0.8) elde edildiği görülmektedir. Bazı organik bileşiklerin girişim etkileri ve karakterizasyon çalışmaları da incelenmiştir. Gün içi ve günler arası çalışmaların bağıl standart sapma değerleri sırasıyla % 1.1 - 1.5 ve % 1.1 - 1.8 aralığında bulunmuştur. Yöntem, musluk suyu numunelerine uygulanmış ve geri kazanımların % 95.3 ile % 99.7 aralığında olduğu bulunmuştur.

Anahtar Kelimeler: 2-fenilfenol, manyetik moleküler baskılanmış polimer, florimetrik tayin, önderiştirme.

1. Introduction

2-phenylphenol or ortho-phenylphenol, is a fungicide and antimicrobial agent mainly used for the post-harvest treatment of fruits and vegetables (Votavová, 2014; Martínez, 2013). It is also used as an active componenet in disinfectants, cosmetics and plastics (Higashi, 2017; Coelhan, 2006). 2-phenylphenol is being considered as moderately toxic in animals however its effect on human remains unknown (Bérubé, 2018). Thus, food, environmental or biological samples may be contaminated upon the usage of 2-phenylphenol. Therefore, quantitative determination of trace levels of 2-phenylphenol in real samples is very important.

Numerous methods such as; colorimetry (Rajzman, 1970), spectrophotometry (Bai, 2012), phosphorimetry (Vallvey, 2003), high-performance liquid chromatography (HPLC) with different detectors (Wei and Ying, 2010; Thompson, 2001; Saad, 2004), gas chromatography-mass spectrometry (GC-MS) (Hong, 2013) and voltammetry (Maleh, 2019) have been reported for the determination of 2-phenylphenol. However, 2-phenylphenol has native fluorescence and to the best of my knowledge, a method depends on the usage of magnetic-molecularly imprinted polymers prior to fluorimetry has not been proposed yet. Fluorescence spectrometry, due to its sensitivity, simplicity and rapidity, has been widely used for the determination of organic and inorganic compounds (Kucukkolbasi and Kilic, 2013; Lakowicz, 2006). Thus, it is important to develop a simple, selective, cheap, rapid and sensitive fluorimetric method based on the usage of magnetic-molecularly imprinted polymers (MMIPs) for the determination of 2-phenylphenol.

Molecularly imprinted polymers (MIPs) are synthetic receptors and selective adsorbents used for the preconcentration, separation and determination of various organic compounds especially in food, biological and environmental samples (Fang, 2021; Azizi and Bottaro, 2020). A growing number of researchers pay attention to use MIPs in various studies due to their selectivity, cheapness, chemical and thermal stability, reusability and mechanical strength (El-Schich, 2020; Liu, 2019). Beside these advantages, the main disadvantage of MIPs is the separation of adsorbent from the sample solution which consumes time (Effting, 2022). In order to solve this problem, magnetic molecularly imprinted polymers have been introduced (Nadali, 2021; Teixeira, 2021).

Especially over the last decade, magnetic molecularly imprinted polymers (MMIPs) have been used as selective adsorbents serving both the advantages of MIPs and magnetic property. MMIPs can be obtained simply by coating the surface of the magnetite particles with a MIP layer (Boontongto and Burakham, 2021). Studies revelead that the magnetization value of MMIP particles are lower than the magnetite particles due to the effect of the formation of the diamagnetic polymeric structure but can be isolated rapidly from the solution with a magnet (Lopez, 2021; Zulfikar, 2022). MIPs were previously used in the chromatographic determination of 2-phenylphenol combined with a UV-detector (Bakhtiar, 2019) but the usage of MMIPs in the separation and detection of fluorimetric 2-phenylphenol has not been reported in the literature to the best of my knowledge. In this study, selective MMIPs have been used for the first time in determination of 2-phenylphenol in tap water samples.

In the present study, a method based on the selective separation and preconcentration of 2-phenylphenol in tap water samples with magnetic molecularly imprinted polymer prior to sensitive fluorimetric detection has been developed. Characterization of the imprinted polymer, optimization of the parameters and the effects of some potential interferences are also evaluated.

2. Materials and Methods

2.1. Materials

2-phenylphenol was purchased from Acros Organics (NJ, USA). Imidacloprid, pirimicarb, carbofuran (98%), thiabendazole (98%), methacrylic acid, ethylene glycol dimethacrylate (97%), 2,2’-azobis(isobutyronitrile), polyvinyl alcohol, chloroform, methanol, 1-Naphthaleneacetic acid, $FeCl_2.4H_2O$, $FeCl_3.6H_2O$, HCl and NaOH were purchased from Merck (St. Louis, MO, USA). Thifensulfuron-methyl (97%), chlorothalonil (98%) and tebuconazole (98%) were purchased from TCI (Portland, OR, USA). 1-naphthol and thiram were purchased from Alfa Aesar (Haverhill, MA, USA). Ultrapure water was used in the studies (Millipore, Bedford, MA, USA).

Stock standard solution (1000 mg L^{-1}) of 2-phenylphenol was prepared in methanol. Stock standard solution was diluted with water and methanol to prepare the working standard solutions. All solutions were stored at 4°C in refrigerator.

2.2. Instrumentation

A RF-5301 PC spectrofluorometer was used for the fluorimetric analysis of 2-phenylphenol (Shimadzu, Japan). Spectrum Two FTIR spectrometer (Perkin-Elmer, USA) was used for determining Fourier transform infrared spectra of the samples. Apreo S LoVac scanning electron microscope (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) (Thermo Scientific, USA) was used for determining the morphologies and elemental analysis of magnetic-molecularly imprinted polymers. Magnetization values were determined with a Lakeshore 7407 vibrating sample magnetometer (VSM) (Lakeshore, USA). Presicion balance was used for all weight measurements (Ohaus, USA). Thermoregulated water bath was used in the synthesis of the magnetic-molecularly imprinted polymers (Stuart, UK).

2.3. Synthesis of magnetite (Fe_3O_4) particles

Magnetite particles were prepared via the coprecipitation of Fe^{2+} and Fe^{3+} ions (Chen and Li, 2013). In order to obtain magnetite particles, 0.01 mol $FeCl_2.4H_2O$ and 0.02 mol $FeCl_3.6H_2O$ were dissolved in 100 mL of ultrapure water. The solution was degassed with nitrogen and the temperature was adjusted to ~80°C. 50 mL, 2 M NaOH (aq) was added drop by drop to the system and the black magnetite particles were observed immediately. Magnetic particles were separated with a magnet and washed with ultrapure water before using in the experiments.

2.4. Synthesis of magnetic-molecularly imprinted polymers (MMIPs)

In the synthesis of MMIP particles, methacrylic acid, ethylene glycol dimethacrylate, 2,2’-azobis(isobutyronitrile) and saturated polyvinyl alcohol solution were used as the functional monomer, cross-linker, chemical initiator and dispersant respectively. Methacrylic acid was chosen as functional monomer due to its ability to form hydrogen bonds with the template. At first, 0.5 mmol 2-phenylphenol was dissolved in 20 mL chloroform and 2.0 mmol methacrylic acid was added to the solution for obtaining the pre-assembly solution. Then, 5 mmol ethylene glycol dimethacrylate was added to the solution. 1 g magnetite (mixed with 5.0 mL oleic acid in a separate flask) was added to the solution.

In the last step, saturated polyvinyl alcohol solution and 0.1 g 2,2’-azobis(isobutyronitrile) were added to the mixture and stirred at 55°C under nitrogen gas for 5 hours (He, 2014).

The synthesized magnetic molecularly imprinted polymers (MMIPs) were separated from the solution with a magnet, washed with methanol and dried in an oven at 80 °C.

2-phenylphenol was extracted from MMIPs washing with methanol and methanol : acetic acid (9:1) successively until it was not detected with spectrofluorimetry. The magnetic non-imprinted polymers (MNIPs) were also synthesized with the same procedure without using the template molecule.

3. Results and Discussion

3.1. Re-binding and recovery of 2-phenylphenol using MMIP

For re-binding of 2-phenylphenol; 5 mL, 200 μg L^{-1} 2-phenylphenol in ultrapure water (with different pH values) was shaken with 100 mg MMIP for 20 minutes at room temperature. Magnetic polymer was separated from the solution with a magnet and 2-phenylphenol was determined with spectrofluorimetry.

Effect of initial pH on the re-binding of 2-phenylphenol was investigated. As shown in Figure 1, the optimum pH was determined as 7 with the quantitative re-binding efficiency of 99.1±0.7% (n=3).

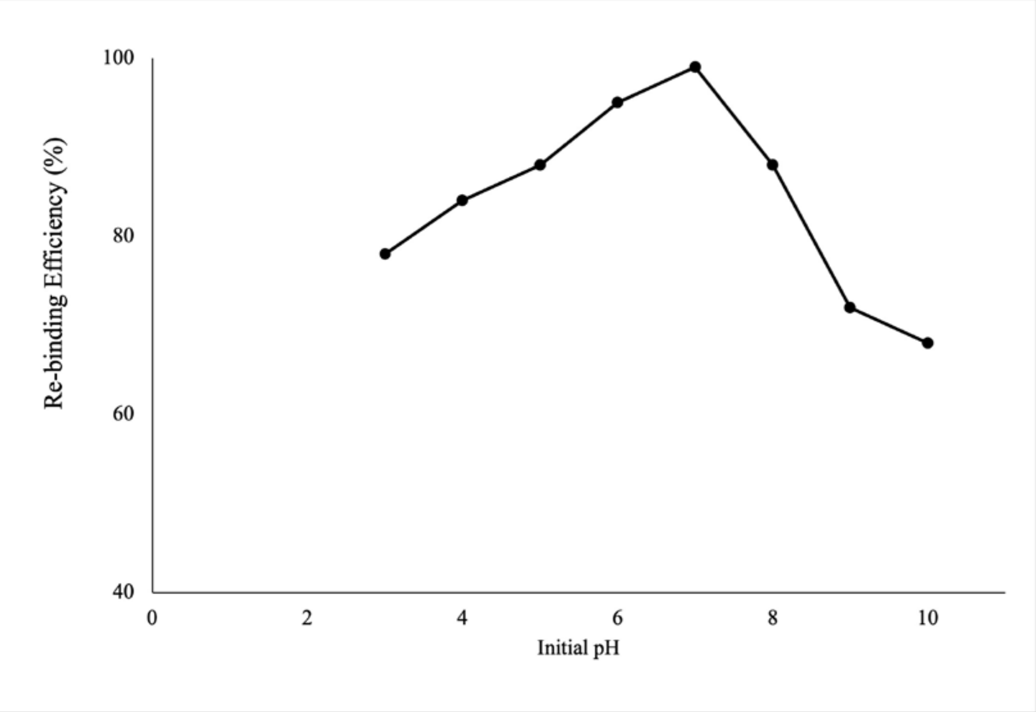

Figure 1. Effect of initial pH on re-binding (amount of polymer: 100 mg, sample volume: 5 mL, initial 2-phenylphenol concentration: 0.2 mg L^{-1}, contact time: 20 minutes, pH: 3-10).

For recovery of 2-phenylphenol; at first re-binding was executed with shaking 5 mL, 200 µg L^{-1} 2-phenylphenol in ultrapure water (pH~7) with 100 mg MMIP for 20 minutes. After sorption of 2-phenylphenol, MMIP was separated from the solution with a magnet and 5 mL fresh methanol added onto MMIP. MMIP was shaken with methanol for 20 minutes in order to recover template which was determined with spectrofluorimetry. The recovery was calculated as 99.2±0.6% (n=3).

The imprinting factor (IF), α, determines the success of the creation of the imprinted sites on the surface of the polymer and can be defined as;

$$\alpha = \frac{Q_{MMIP}}{Q_{MNIP}} \tag{1}$$

and Q_{MMIP} (µmol g^{-1}) and Q_{MNIP} (µmol g^{-1}) indicate the amount of 2-phenylphenol adsorbed by MMIP and MNIP, respectively. In order to determine the imprinting factor; 5 mg MNIP and MMIP were shaken with 5 mL of 100 µg L^{-1} 2-phenylphenol solution in ultrapure water (pH~7) for 1 hour. Q_{MMIP} and Q_{MNIP} were calculated as 0.0494 µmol g^{-1} and 0.0265 µmol g^{-1}, respectively. Thus, the imprinting factor was found to be 1.87.

3.2. Effect of contact time on re-binding and recovery of 2-phenylphenol

The effect of contact time on re-binding and recovery of 2-phenylphenol can be shown in Figure 2. As observed, both re-binding and recovery of 2-phenylphenol were both completed in 20 minutes and it can be concluded that the developed method was rapid for the fluorimetric determination of trace levels of 2-phenylphenol using MMIP.

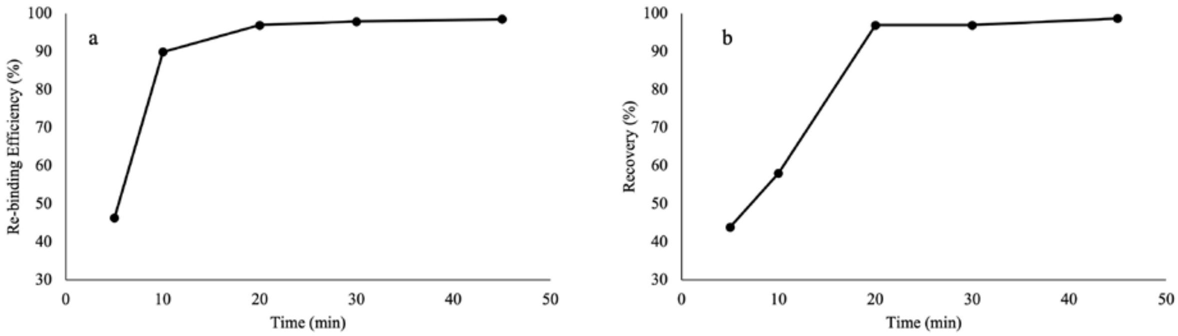

Figure 2. Effect of time on a) re-binding and b) recovery (amount of polymer: 100 mg, sample volume: 5 mL, initial 2-phenylphenol concentration: 0.2 mg L^{-1}, time: 5-45 minutes).

3.3. Effect of MMIP dosage on re-binding of 2-phenylphenol

The amount of MMIP used in different sample volumes is the main factor affecting the sorption efficiency. Thus, the mimimum MMIP dosage was determined to ensure the quantitative re-binding of 2-phenylphenol. Figure 3 shows that a minimum of 12 g L^{-1} MMIP should be used for the quantitative sorption. Under this dosage, the amount of polymer is not sufficient for quantitative sorption and the active sites on the surface of the polymer increases as the amount of polymer increases causing an increase in the re-binding efficiency. Beyond 12 g L^{-1}, the adsorption capacity remains constant and in order to avoid consuming the excess amount of MMIP, 12 g L^{-1} MMIP can be used for the quantitative sorption of 2-phenylphenol.

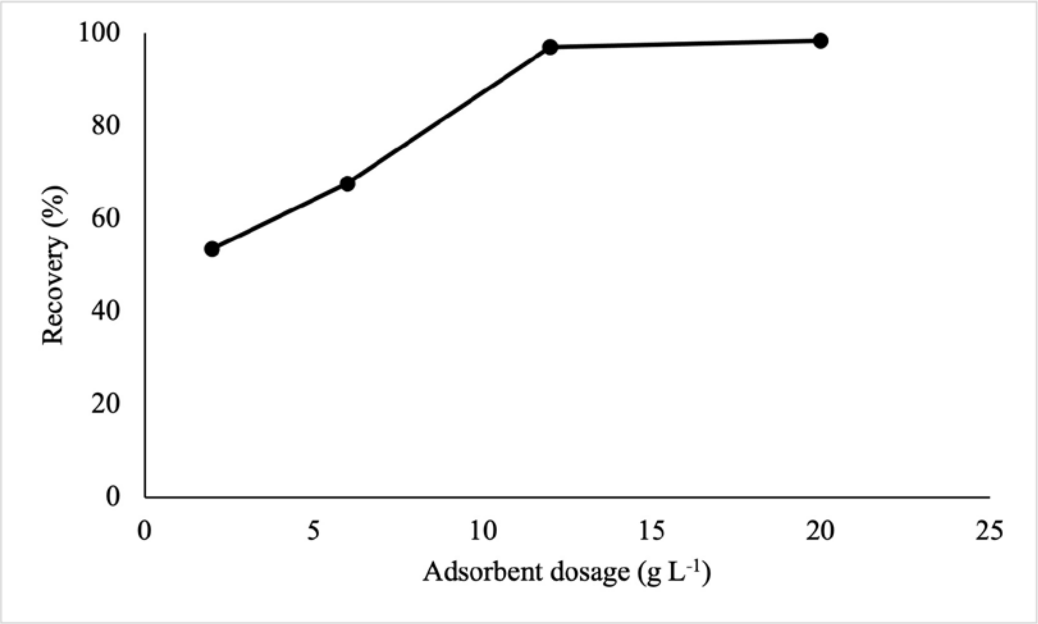

Figure 3. Effect of adsorbent dose (initial 2-phenylphenol concentration: 0.2 mg L^{-1}, sample volume: 5 mL, sorption time: 20 minutes, polymer amount: 10-100 mg).

3.4. Characterization of the adsorbent

FT-IR specta of MMIP and magnetite particles can be shown in Figure S1. FT-IR spectrum of MMIP involves the peaks at 2930 cm^{-1}, 1720 cm^{-1} and 1140 cm^{-1} indicating the C-H streching, C=O stretching and C-O stretching, respectively which confirm the formation of the polymer. Figure 4 shows the SEM-EDX analysis of MMIP particles. Uniform spherical MMIP particles with an average diameter of approximately 35 nm were obtained in SEM image. EDX spectrum and mapping analysis used for the elemental analysis of the synthesized polymer particles. According to EDX analysis, iron (Fe), oxygen (O) and carbon (C) elements were detected on the surface of the particles with the percentages of 68%, 25% and 7%, respectively. As magnetite (Fe_3O_4) consisted of only Fe and O, EDX results confirmed the successful synthesis of MMIP particles.

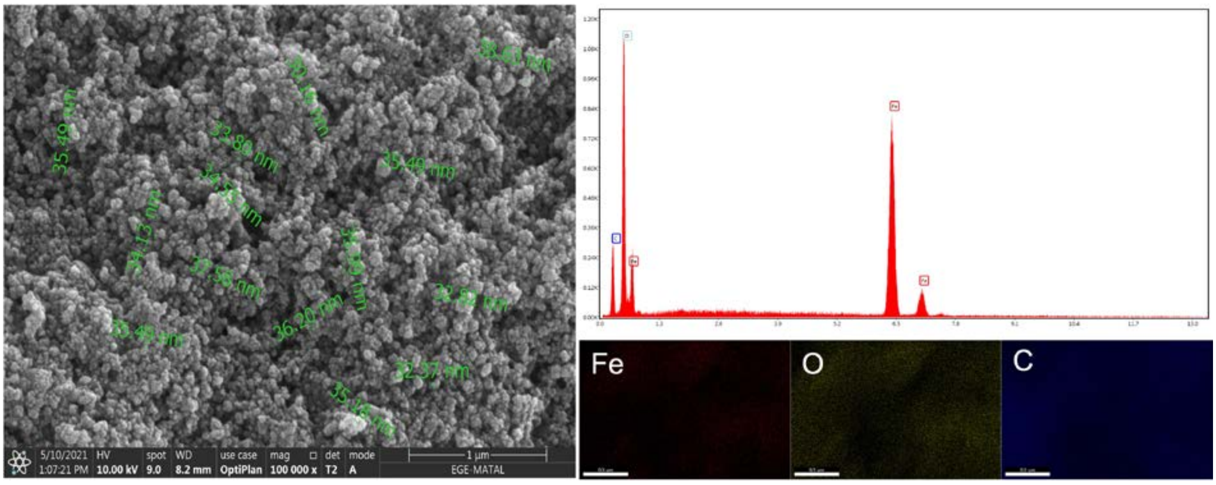

Figure 4. SEM-EDX analysis of MMIP (applied voltage: 10 kV for SEM, 20 kV for EDX analysis, working distance: 8.2 mm, magnification: 100000x).

Vibrating sample magnetometer (VSM) analysis was used for the determination of the magnetic properties of magnetite and MMIP particles. According to Figure 5, magnetite particles possessed a saturation magnetization value (M_s) of 52.7 emu g^{-1} whereas MMIP particles had a M_s value of 2.6 emu g^{-1}. The formation of the diamagnetic polymer layer over the surface of the magnetite particles was accompanied by a drastic decrease in Ms value (Shahri and Azizi, 2017).

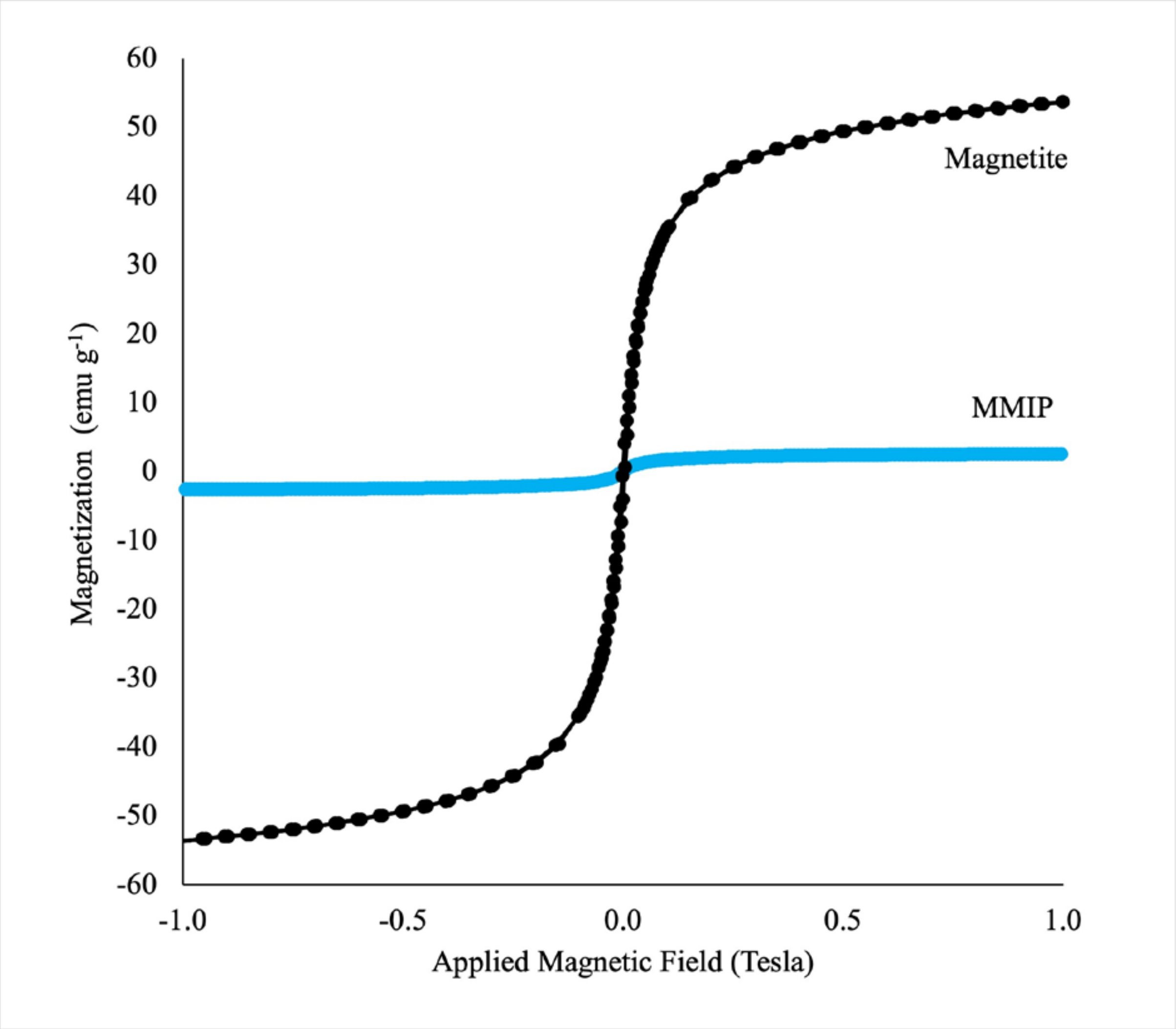

Figure 5. VSM analysis of magnetite and MMIP (applied magnetic field: -1 to 1 Tesla).

3.5. Scatchard analysis for MMIP and MNIP

Scatchard analysis was used for determining the capacities of the polymers and the type of the distribution of the binding sites of the molecularly imprinted polymers (Ho, 2005). In order to create Scatchard analysis plots; 10 mg polymer was shaken with 5 mL of various initial concentration of 2-phenylphenol solution (0.05-0.50 mg L^{-1}) in ultrapure water (pH~7) for 1 hour. After sorption, polymer was separated from the solution with a magnet and the amount of 2-phenylphenol in the solution was determined with spectrofluorimetry.

In Scatchard analysis model, Q is the amount of 2-phenylphenol adsorbed by the polymer (μmol g^{-1}), C is the equilibrium concentration (μmol L^{-1}), Q_{max} is the maximum number of binding sites (μmol g^{-1}) and K_d is the equilibrium dissociation constant (μmol L^{-1}).

As shown in Figure 6, in Scatchard plot for MMIP, two different linear regions were observed which indicate the heterogeneous distribution of binding sites on the polymer and therefore two different types of binding sites were responsible for the sorption of 2-phenylphenol.

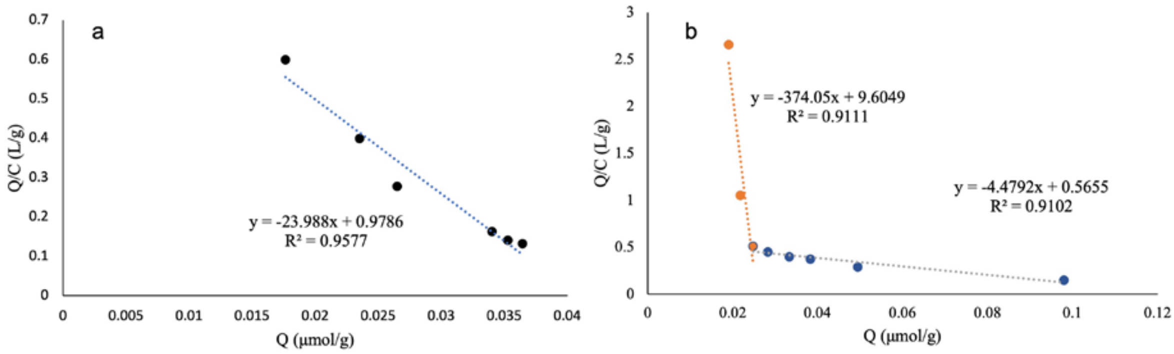

Figure 6. Scatchard analysis of a) MNIP and b) MMIP (amount of polymer: 10 mg, sample volume: 5 mL, initial concentration of 2-phenylphenol solution: 0.05-0.50 mg L $^{-1}$, sorption time: 60 minutes).

However, for MNIP, one linear region indicates a homogeneous binding site responsible for the sorption of 2-phenylphenol (Ho, 2005). Parameters of Scatchard analysis were calculated using the slope and intercept of the plots and the results are shown in Table 1.

Table 1. Parameters of the Scatchard analysis.

	Q_{max1} (μmol g^{-1})	Q_{max2} (μmol g^{-1})	K_{d1} (μmol L^{-1})	K_{d2} (μmol L^{-1})
MNIP	0.04	-	0.04	-
MMIP	0.13	0.03	0.22	0.003

3.6. Selectivity of MMIP

The selectivity of the synthesized MMIP was investigated using 1-naphthol and 1-naphthalene acetic acid that have similar functional groups and structures to 2-phenylphenol. 5 mL of 250 μg L^{-1} 2-phenylphenol solution in ultrapure water (pH~7), individually and as a binary mixture of the studied compounds were shaken with 5 mg MMIP or MNIP. The selectivity of MMIP was determined using the following equations;

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \tag{2}$$

$$k = \frac{K_d(2\text{−phenylphenol})}{K_d(\text{competitor})} \tag{3}$$

$$k' = \frac{k_{MMIP}}{k_{MNIP}} \tag{4}$$

where K_d is the distribution coefficient (L g^{-1}), C_0 is the initial concentration of the compound (μg mL^{-1}), C_e is the final concentration of the compound after sorption (μg mL^{-1}), V is the sample volume (mL), m is the amount of polymer (mg), k is the selectivity coefficient and k' is the relative selectivity coefficient. The results were shown in Table 2 and selectivity parameters signified that the specific binding sites were available on MMIP which is capable of recognizing 2-phenylphenol molecules with their functional groups, size and shape.

Table 2. The selectivity of MMIP.

Pesticide	**MMIP**		**MNIP**		
	K_d (L/g)	k	K_d (L/g)	k	k'
2-phenylphenol	0.92	-	0.37	-	-
1-Naphthol	0.43	2.14	0.25	1.48	1.45
1-Naphthaleneacetic acid	0.52	1.77	0.68	0.54	3.28

3.7. Analytical figures of merit

2-phenylphenol solution in ultrapure water (pH~7) has an excitation wavelength (λ_{ex}) of 245 nm and a maximum emission wavelength (λ_{em}) of 420 nm. The calibration graph of 2-phenylphenol in ultrapure water (pH~7) is linear in the range of 5 - 250 µg L^{-1} with an equation of $y = 2594.6x + 14827$ and a correlation coefficient (R^2) of 0.9973 (n=3).

2-phenylphenol solution in methanol has excitation and maximum emission wavelengths of 285 nm and 336 nm, respectively. The calibration graph of 2-phenylphenol in methanol is also linear for 5 - 250 µg L^{-1} with an equation of $y = 3197.7x + 44880$ with a correlation coefficient of 0.9945 (n=3).

Fluorescence spectra and calibration graphs of 2-phenylphenol both in ultrapure water (pH~7) and methanol are shown in Figure S2.

Limit of detection (LOD) and limit of quantification (LOQ) were calculated using the equations;

$LOD = \frac{\sigma}{S} \times 3$ (5) and $\mathrm{LOQ} = \frac{\sigma}{\mathrm{S}} \times 10$ (6) where σ is the standard deviation of the responses of the blank solution and S is the slope of the calibration curve.

For re-binding studies, LOD and LOQ were calculated as 1.28 µg L^{-1} and 4.28 µg L^{-1}, respectively, whereas LOD and LOQ were determined as 1.09 µg L^{-1} and 3.66 µg L^{-1}, respectively, for recovery studies.

In order to determine the precision of the developed method, relative standard deviations (RSDs) of intra-day and inter-day precisions of recovery studies were determined for 25, 50 and 100 µg L^{-1} 2-phenylphenol solutions. Five repeated measurements of samples on the same day were used for determining the intra-day precision whereas the inter-day precision was determined by measuring the sample once a day for five consecutive days. RSD values of intra-day and inter-day studies were found to be in the range of 1.1 - 1.5 % and 1.1 - 1.8 %, respectively. Considering the precision, LOD and the linear range of the calibration graphs, the developed method expected to be an alternative method for the determination and preconcentration of 2-phenylphenol. Although there are a limited number of published methods for 2-phenylphenol detection, general performance parameters of the methods are shown in Table 3. As it is obvious with the LOD, the proposed method is better than majority of the proposed methods.

Table 3. Comparison of published methods for the determination of 2-phenylphenol with the present work.

Working range	Limit of Detection	Method	Sample Matrice	Reference
0.01–520 µM	6.0 nM	nano-Fe_3O_4/ionic liquid paste electrode based voltammetry	orange, lemon and water	Maleh, 2019
0.5–4.0 mg L^{-1}	30.0 µg L^{-1}	solid-phase spectrophosphorimetry	water and vegetables	Vallvey, 2003
1-10 mg L^{-1}	500.0 µg L^{-1}	solid-phase extraction- ultraviolet spectrophotometry	vegetables and fruits	Bai, 2012
-	5.0 µg kg^{-1}	high-performance liquid chromatography-fluorescence detection	apple and orange	Saad, 2004
10-1000 µg L^{-1}	1.09 µg L^{-1}	magnetite molecularly imprinted polymer-fluorescence detection	tap water	This study

3.8. Reusability of MMIP

Ten cycles of sorption-recovery procedures were applied to the same MMIP in order top determine the reusability of the polymer. Re-binding efficiencies and recovery values were determined as 99.0±0.7 and 98.8±0.8 (n=10), respectively. Therefore, the same MMIP can be used at least ten times for determination of 2-phenylphenol.

3.9. Interference effects

The possible interference effects of different pesticides such as; tebuconazole, imidacloprid, thiram, pirimicarb, carbofuran, thifensulfuron-methyl, chlorothalonil and thiabendazole on the determination of 2-phenylphenol were investigated. For the investigation of interference effect, 5 mL of 10 µg L^{-1} 2-phenylphenol solution with different concentrations of interferents was shaken with 100 mg MMIP for 20 minutes. After re-binding, MMIP was separated with a magnet and 5 mL methanol was added onto MMIP and shaken for 20 minutes for recovery process. The tolerable ratios of all investigated pesticides were found to be 1000-fold. Thus, the developed method was ideal for the determination of trace levels of 2-phenylphenol in the presence of widely used pesticides due to the selectivity and sensitivity of the method.

3.10. Analytical application

The proposed method was applied to tap water samples for the determination of trace levels of 2-phenylphenol. At first, tap water was filtered through polytetrafluoroethylene membrane. After adjusting the pH value to 7, 25 mL of tap water was shaken with 300 mg MMIP for 20 minutes for the re-binding of 2-phenylphenol. After sorption, MMIP was separated from the solution with a magnet and 5.0 mL of fresh methanol was added onto MMIP and shaken for 20 minutes for the recovery of 2-phenylphenol. 2-phenylphenol was not detected in the samples (λ_{ex}=285 nm and λ_{em} =336 nm) therefore spike addition was applied and the recoveries of samples were obtained in the range of 95.3 and 99.7 %. The preconcentration factor of the analysis was determined as 5 and the results are described in Table 4.

Table 4. Determination of 2-phenylphenol in tap water samples.

Sample	Added (µg/L)*	Found (µg/L)*	Total Recovery of 2-phenylphenol Added to the Original Sample (%)
Tap water	-	<LOD**	-
	10.0	9.5±0.3	95.3±2.5
	25.0	24.8±0.4	99.1±1.4
	50.0	49.9±1.0	99.7±2.0

*(n=3)

**LOD: Limit of Detection

4. Conclusion

The present work describes a method which was consisted of rapid preconcentration and fluorimetric determination of 2-phenylphenol. Selective separation and preconcentration of 2-phenylphenol was achieved with reusable magnetic molecularly imprinted polymers whereas native fluorescence of the analyte was used for sensitive detection. The developed method was rapid and completed in 40 minutes. Selectivity parameters showed that the specific binding sites were available on the imprinted polymer which was capable of recognizing 2-phenylphenol molecules with their functional groups, size and shape. Scatchard analysis revealed the heterogeneous distribution of binding sites for imprinted polymer and homogeneous binding site for non-imprinted polymer. Limit of detection (LOD) of the method was found to be 1.09 µg L^{-1} and the imprinting factor was found to be 1.87. The method was applied to tap water samples and quantitative recoveries were obtained.

Ethics in Publishing

There are no ethical issues regarding the publication of this study.

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