Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.913205

55 (2015) 278–283
June

Taylor & Francis
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Selective detection of TNT using molecularly imprinted polymer microsphere

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Received 18 September 2013; Accepted 4 April 2014

ABSTRACT

The rapid detection of nitroaromatic explosive in low concentration sample or complex matrices is of importance. In this paper, 2,4,6-trinitrotoluene (TNT) molecularly imprinted polyvinyl alcohol microspheres, MIP-CPVA, are synthesized in inverse suspension system using TNT as template, PVA as functional polymer, and glutaraldehyde as cross-linker. The MIP-CPVA possesses high affinity, specific recognition ability, and excellent selectivity towards TNT. The saturated adsorption capacity could reach to 10.62 mg g^{-1}, and the selectivity coefficients relative to DNT is 12.44. In additional, MIP-CPVA can be used as the column packing of gas chromatograph to separate and detect nitroaromatic, and the result is very satisfactory.

Keywords: Molecularly imprinted polymer; 2,4,6-trinitrotoluene; Polyvinyl alcohol; Gas chromatograph; Separation

1. Introduction

The chemical compound 2,4,6-trinitrotoluene (TNT) is a widely used nitroaromatic explosive. At the same time of use, it is released into the soil and ground water mainly through military-related activities, such as munitions manufacturing, packing, and storage. The discharge of TNT resulted in contamination of large tracts of soils and groundwater over the entire world. TNT is a mutagen and a Group C human carcinogen. Exposure to TNT is known to cause rashes, skin hemorrhages, mucus, and blood disorders. Due to its toxic and mutagenic effects to many living organisms, increasingly rigorous limits on the released capacity of TNT have been established worldwide. The rapid detection of TNT in low concentration samples or complex matrices is of importance. In the detection process, direct measurement using sensors and subsequent measurement after preconcentration is employed usually [1–5]. Among these measurement methods, the imprinted polymer is the most effective and important component part.

The molecular imprinting technology that can offer specific molecular recognition sites in solid materials is one of the most efficient methods. The molecular imprinted polymers (MIPs) have been utilized as molecular recognition materials in many scientific and technical fields, such as solid-phase extraction, chromatograph separation, membrane separations, sensors, drug releases, and catalysts [6–13].

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1944-3994/1944-3986

Polyvinyl alcohol (PVA) is a kind of water-soluble polymer, and utilized in many of fields [14–17]. In PVA molecular chains, there are a great number of isolated hydroxyl functional groups, which can form hydrogen bond with TNT by ways of hydroxyl and nitro. The hydroxyl also can react with aldehyde group to realize the cross-linking of PVA molecular chains.

In this paper, molecularly imprinted polymer microspheres, MIP-CPVA, are synthesized using TNT as template, PVA as functional polymer, and glutaraldehyde as cross-linker. The adsorption and recognition ability of MIP-CPVA towards TNT is researched.

2. Experimental

2.1. Materials and instruments

Polyvinyl alcohol (PVA, polymerization degree of 2,200) is purchased from the Sanwei Chemical Engineering Ltd. (Shanxi, China, AR grade). The TNT is obtained from the Chemical Engineering Department of the North University of China. All other chemicals are purchased from the Beijing Chemical Plant (Beijing, China, AR grade).

The instruments used in this study are as follows: Unic-2,602 UV–vis spectrophotometer (Unic Company, American), Perkin–Elmer 1,700 infrared spectrometer (FTIR, Perkin–Elmer Company, USA), LEO-438VP scanning electronic microscope (SEM, LEO Company, UK), THZ-92C constant temperature shaker (Shanghai Boxun Medical Treatment Equipment Factory, China), and 7890A gas chromatograph (Agilent Company, USA).

2.2. Preparation of MIP-CPVA

Disperser Span 60 (Sorbitan monostearate) is dissolved in liquid paraffin to constitute the oil phase (continuous phase). An aqueous PVA solution is mixed with TNT and glutaraldehyde solution to constitute the water phase (dispersed phase). The water phase is poured into the oil phase, and the system is fully dispersed by stirring to form an inverse suspension system. After adding HCl solution as the catalyst, the cross-linking reaction (aldolization) and balling process are carried out for 7 h at 65℃. Finally, the template is removed by Soxhlet extraction with acetone for 48 h, and semitransparent imprinted microspheres MIP-CPVA with a mean diameter of 150 μm are obtained. The preparation scheme is shown in Fig. 1.

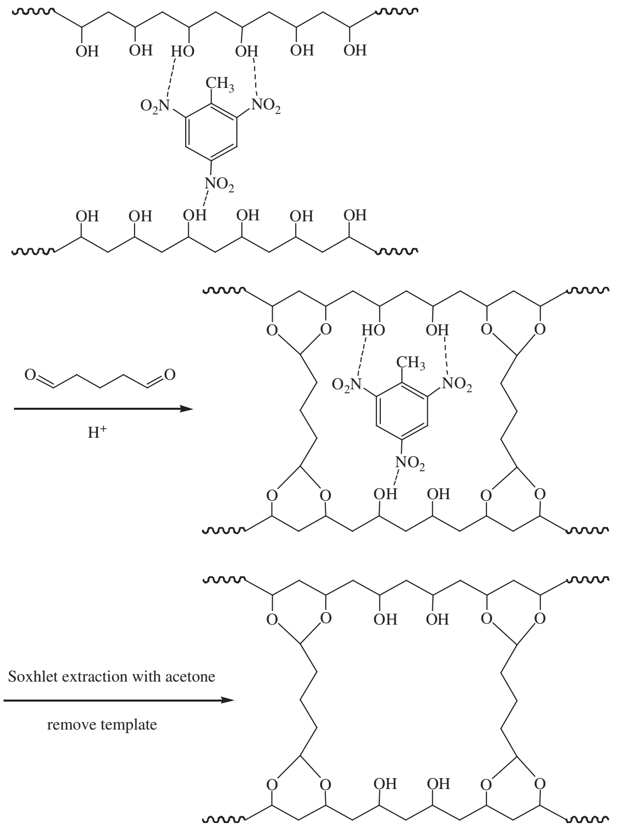

Fig. 1. Preparation scheme of MIP-CPVA.

For researching the imprinted effect, the non-imprinted polymer (NIP-CPVA) is prepared using the same method in the absence of the template TNT.

The infrared spectrum of MIP-CPVA is determined in order to confirm the chemical structure. The SEM image is used to observe the surface morphology.

2.3. Measurement of kinetic adsorption curve

About 0.1 g of MIP-CPVA is directly introduced into a conical flask, into which 250 mL of the aqueous TNT solution with an initial concentration (C_0) of 100 mg L^{-1} is added. The conical flask is then shaken at a presettled temperature. At different times, the concentration (C_t) of the TNT in solution is determined using UV–vis spectrophotometer. The adsorption capacity (Q) is calculated according to Eq. (1).

$$Q = V(C_0 - C_t)/m \tag{1}$$

where Q (mg g^{-1}) is the adsorption capacity; V(L) is the volume of the TNT solution; and m (g) is the weight of the absorbent MIP-CPVA.

2.4. Measurement of adsorption isotherm

About 0.01 g of MIP-CPVA is directly introduced into several conical flasks, into which 25 mL of the aqueous TNT solution with different initial concentrations (C_0) of 20, 40, 60, 80, and 100 mg L^{-1} are, respectively, added. These conical flasks are then shaken at a presettled temperature. After reaching the adsorption equilibrium, the equilibrium concentrations (C_e) of the TNT solutions are determined using UV–vis spectrophotometer. The equilibrium adsorption capacity (Q_e) is then calculated according to Eq. (2).

$$Q_e = V(C_0 - C_e)/m. \tag{2}$$

2.5. Selectivity studies

In order to show the selectivity of MIP-CPVA towards TNT, competitive adsorptions of MIP-CPVA towards TNT with respect to DNT is also carried out. The binary mixed solution of DNT/TNT is prepared. In this mixed solution, the concentrations of DNT and TNT are all 100 mg L^{-1}. After adsorption equilibrium is reached, the concentrations of DNT and TNT in the remaining solutions are determined with gas chromatograph, respectively.

Distribution coefficients of DNT and TNT are calculated by Eq. (3).

$$K_d = \frac{Q_e}{C_e} \tag{3}$$

where K_d represents the distribution coefficient (L/g); Q_e (mg g^{-1}) is the equilibrium adsorption capacity; and C_e (mg L^{-1}) is the equilibrium concentration.

The selectivity coefficient of MIP-CPVA for TNT with respect to DNT can be obtained from the equilibrium binding data according to Eq. (4)

$$k = \frac{K_d(\text{TNT})}{K_d(\text{DNT})} \tag{4}$$

where k is the selectivity coefficient. The value of k allows an estimation of selectivity of MIP-CPVA for TNT.

3. Results and discussion

3.1. Characterization of MIP-CPVA

The FTIR spectrum of MIP-CPVA is shown in Fig. 2.

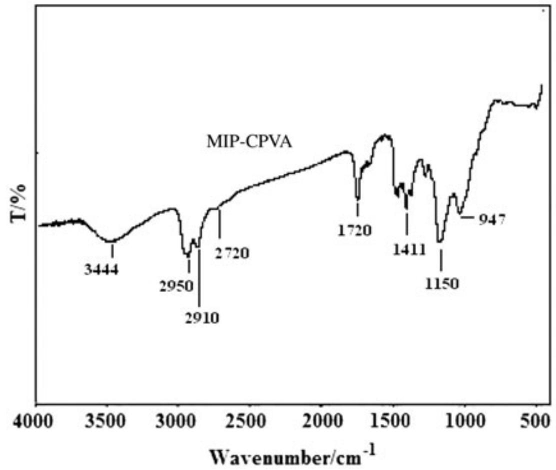

Fig. 2. FTIR spectrum of MIP-CPVA microspheres.

In the FTIR spectrum of MIP-CPVA, the absorption band at 1,150 cm^{-1} is the characteristic absorption band of C–O–C, the absorption band at 3,444 cm^{-1} is the characteristic absorption band of –OH. All of these absorption bands indicate that the aldolization reaction between PVA and glutaraldehyde is carried out, and MIP-VPVA is formed.

The SEM image of MIP-CPVA is shown in Fig. 3. It can be seen that the microspheres showed good sphericity, and particle size distribution is relatively uniform.

3.2. Kinetic adsorption curve

The kinetic adsorption curve is shown in Fig. 4.

The adsorption of MIP-CPVA towards TNT reaches to equilibrium in 8 h, and the saturated adsorption capacity could reach to 10.62 mg g^{-1}. It is implied that MIP-CPVA possesses strong adsorption ability and affinity towards TNT. The high affinity

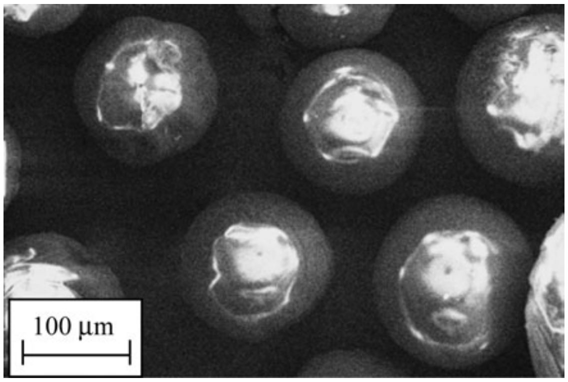

Fig. 3. SEM image of MIP-CPVA microspheres.

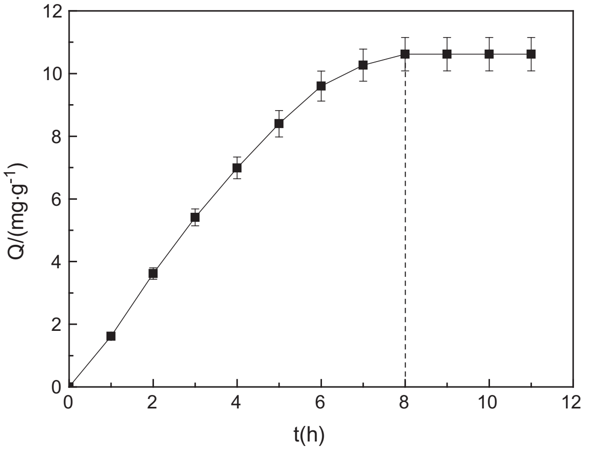

Fig. 4. Kinetic adsorption curve. Temperature: 25℃; pH = 6; initial concentration of TNT: 100 mg L^{-1}.

attributes to the hydrogen bond interaction between PVA and TNT.

3.3. *Adsorption isotherm*

The adsorption isotherm of MIP-CPVA towards TNT is shown in Fig. 5. It can be seen that the equilibrium adsorption capacity increases rapidly with the increase of equilibrium concentrations.

Freundlich adsorption equation and its logarithms form are follows:

$$Q_e = kC_e^n \quad (5)$$

$$\ln Q_e = \ln k + n \ln C_e \quad (6)$$

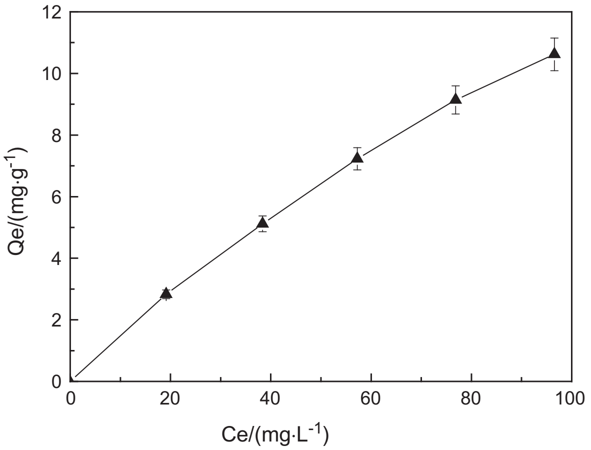

Fig. 5. Adsorption isotherm of MIP-CPVA towards TNT. Temperature: 25℃; pH = 6; Adsorption time: 8 h.

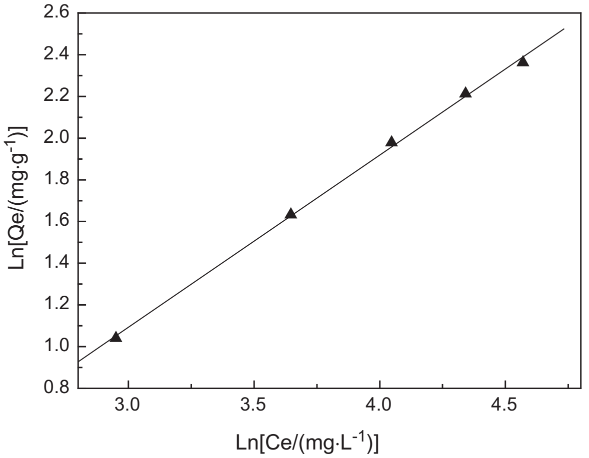

Fig. 6. Plot of $\ln Q_e$ vs. $\ln C_e$.

The data in Fig. 5 are treated using Freundlich adsorption equation, and the straight lines are displayed in Fig. 6. Linear regression is performed according to the logarithmic form, and the linear regression coefficient is 0.9987. The curve of the lnQ_e vs. lnC_e fit satisfactorily to Freundlich equation. This indicated that the adsorption of MIP-CPVA towards TNT belongs to Freundlich-type adsorptions, and is a kind of typical monomolecular layer adsorptions.

3.4. *Adsorption selectivity*

The adsorption isotherms of MIP-CPVA towards DNT and TNT in mixed solution are shown in Fig. 7.

It can be seen that the saturated adsorption capacity of MIP-CPVA towards TNT is higher than that of MIP-CPVA towards DNT, and the adsorption capacity of MIP-CPVA towards DNT is nearly zero. The only difference between TNT and DNT is one nitro group, but the adsorption ability of MIP-CPVA towards TNT is stronger than that of MIP-CPVA towards DNT in batch adsorption experiment. The above facts display fully the MIPs' excellent ability, and MIP-CPVA has high affinity, high recognition ability, and special selectivity towards TNT. Further data will be given in Table 1.

Competitive adsorptions of MIP-CPVA towards DNT and TNT are also researched in static systems. Table 1 summarizes the data of the distribution coefficients K_d, selectivity coefficients k, and relative selectivity coefficients k'.

It can be seen that the selectivity coefficients of MIP-CPVA TNT is 12.44. This suggests that the adsorption recognition ability of MIP-CPVA towards TNT is far stronger than that towards DNT. The

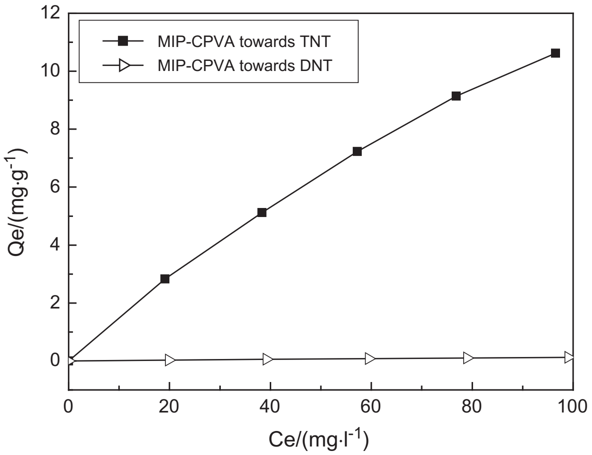

Fig. 7. Adsorption isotherms of MIP-CPVA towards DNT and TNT. Temperature: 25℃; pH = 6; Adsorption time: 8 h.

Table 1
Distribution coefficient and selectivity coefficient data

	K_d/(L g^{-1})		
Adsorbent	TNT	DNT	*k*
MIP-CPVA	0.112	0.009	12.44

reason for this is that the cavities imprinted by TNT are nonmatched to DNT in size, shape, and spatial arrangement of combining sites, and it is difficult for DNT to produce easily hydrogen bond interaction with PVA under the competition of TNT. This result in the adsorption capacity of MIP-CPVA towards DNT is very poor.

3.5. Practical application

In order to demonstrate the practical application value, the MIP-CPVA, NIP-CPVA, commercial HP-1, and QF-1 are used as column packing of gas chromatograph to analyze the explosive including DNT and TNT. The operational conditions are as follows: Apparatus model: Agilent 7890A gas chromatograph; Vaporizing chamber temperature: 220℃; Column temperature: 200℃; Carrier gas flow rate: 1.85 mL min^{-1}. The gas chromatograph figure and measurement results are shown in Fig. 8 and Table 2.

It can be seen that the NIP-CPVA could not separate DNT and TNT fully and the retention time of DNT and TNT is 5.13 and 5.44 min, respectively. While MIP-CPVA used as column packing of gas chromatograph, the DNT and TNT could be separated fully. The retention time of DNT and TNT is 6.42 and 10.54 min, respectively. The separation effect is better than these two commercial GC columns. The methanol is used as internal standard. The concentration of DNT and TNT to be calculated is 29.57 and 39.18 mg L^{-1}, respectively. This value is very close to the actual concentrations (30.00 and 40.00 mg L^{-1}). As for MIP has certain retention time for DNT in gas chromatography experiment, this may be related to the high temperature of experiment. High temperature may make a certain extent changes of the imprinting caves structure, and this will affect the adsorption performance of the imprinted material. But even so, the molecularly imprinted materials prepared in this study still showed good separation identification performance when used as column packing. This indicated that this imprinted material MIP-CPVA could be used as the column packing of gas chromatograph to separate and detect nitroaromatic.

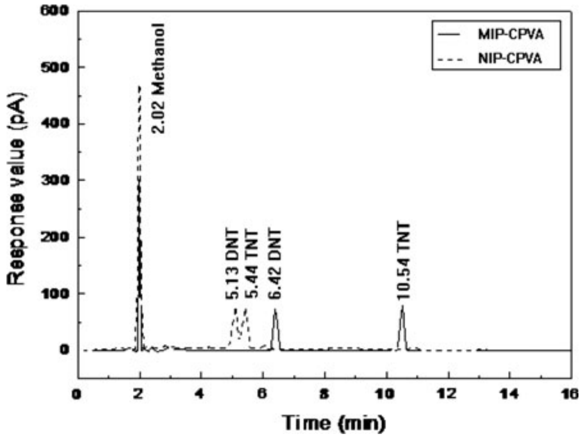

Fig. 8. The gas chromatograph figure.

Table 2
Gas chromatograph results

	Retention time/(min)		Concentration/ (mg L^{-1})	
Column packing	DNT	TNT	DNT	TNT
MIP-CPVA	6.42	10.54	29.57	39.18
NIP-CPVA	5.13	5.44	28.56	38.59
HP-1	5.72	7.35	29.34	39.39
QF-1	1.82	2.27	29.16	38.96

4. Conclusions

TNT molecularly imprinted polymer, MIP-CPVA, is synthesized in inverse suspension system using

TNT as template, PVA as functional polymer, and glutaraldehyde as cross-linker. The MIP-CPVA possesses high affinity, specific recognition ability, and excellent selectivity towards TNT. The selectivity coefficients relative to DNT is 12.44. The most important of all is that this imprinted material MIP-CPVA could be used as the column packing of gas chromatograph to separate and detect nitroaromatic, and the separation and detection results are very satisfactory.

Acknowledgments

This study was supported by the National Scientific Foundation of China (5110423) and Scientific Foundation of Province Shanxi (20130321022-02, 2013021012-3).

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