



## Selective removal of 2,4-dichlorophenoxyacetic acid from water by molecularly-imprinted amino-functionalized silica gel sorbent

Demian Han\*, Wenping Jia, Huading Liang

*Department of Chemistry, Taizhou University, Linhai 317000, China. E-mail: [hdm@tzc.edu.cn](mailto:hdm@tzc.edu.cn)*

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### Abstract

A molecularly-imprinted amino-functionalized sorbent for selective removal of 2,4-dichlorophenoxyacetic acid (2,4-D) was prepared by a surface imprinting technique in combination with a sol-gel process. The 2,4-D-imprinted amino-functionalized silica sorbent was characterized by FT-IR, nitrogen adsorption and static adsorption experiments. The selectivity of the sorbent was investigated by a batch competitive binding experiment using an aqueous 2,4-D and 2,4-dichlorophenol (2,4-DCP) mixture or using an aqueous 2,4-D and 2,4-dichlorophenylacetic acid (DPAC) mixture. The largest selectivity coefficient for 2,4-D in the presence of 2,4-DCP was found to be over 18, the largest relative selectivity coefficient between 2,4-D and 2,4-DCP over 9. The static uptake capacity and selectivity coefficient of the 2,4-D-imprinted functionalized sorbent are higher than those of the non-imprinted sorbent. The imprinted functionalized silica gel sorbent offered a fast kinetics for the extraction/stripping of 2,4-D, 73% of binding capacity (200 mg/L 2,4-D onto 20 mg of imprinted sorbent) was obtained within 5 min and the adsorbed 2,4-D can be easily stripped by the mixture solution of ethanol and 6 mol/L HCl (*V:V* = 1:1). In a test of five extraction/stripping cycles, the adsorption capacity of the sorbent was all above 93% of that of the fresh sorbent. Experimental result showed the potential of molecularly-imprinted amino-functionalized sorbent for selective removal of 2,4-D.

**Key words:** 2,4-dichlorophenoxyacetic acid; molecular imprinting; functionalized silica gel

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### Introduction

2,4-Dichlorophenoxyacetic acid (2,4-D) is extensively used as a plant growth regulator for agricultural and non-agricultural purposes. However, it has been proved to be toxic to human and animals (Garabrant and Philbert, 2002; James and Larry, 2007; Munro et al., 1992). The World Health Organization has recommended 70 µg/L as its maximum permissible concentration in drinking water. Therefore, its presence in water sources for human and animal consumption is highly objectionable. Consequently, the development of reliable methods for the removal of 2,4-D is of particular significance. Several conventional processes, including adsorption (Aksu and Kabasakal, 2005; Hiller et al., 2008), advanced oxidation (Rabindra et al., 2007; Erick et al., 2007) and biological treatment (Santacruz et al., 2005), are commonly applied for the treatment of 2,4-D in contaminated water. Among these processes, adsorption is a very attractive treatment method for the removal of toxics from water (Mohanty et al., 2006; Nabi et al., 2009). The relative advantages of adsorption over other conventional advanced treatment methods are: (1) it can remove both organic as well as inorganic constituents even at very low concentrations, (2)

it is relatively easy and safe to operate, (3) both batch and continuous equipment can be used, (4) there is no sludge formation, (5) the adsorbent can be regenerated and used again, and (6) moreover the process is economical because it requires low capital cost.

Molecular imprinting is an attractive method for the preparation of selective sorbents (Martin-Esteban, 2001; Andersson, 2001; Zhu, 2005). Studies on molecularly imprinted polymers (MIPs) using 2,4-D as template, or analogues thereof (mainly 2,3,4-trichlorophenoxyacetic acid, 2,4,5-T) are well documented over the past years (Legido-Quigley et al., 2007; Baggiani et al., 2004). Haupt et al. (1998) pioneered the studies on 2,4-D imprinted polymers and introduced a polymerisation protocol involving polar protogenic solvents, with the selectivity being confirmed by radioligand binding assays. Baggiani et al. (2001, 2004) reported a few related studies, involving mainly 2,4,5-T templated MIPs as chromatographic stationary phases. Also, SPE cartridges were explored, in view of a suitable application to clean-up and pre-concentrate aqueous samples containing chlorinated phenoxyacids. In these publications, MIPs are synthesized using 4-vinylpyridine as an interacting monomer, ethylendimethacrylate as a cross-linker. Recently, molecularly imprinted sol-gel materials (MISGMs) have been

\* Corresponding author. E-mail: [hdm@tzc.edu.cn](mailto:hdm@tzc.edu.cn)

*jesc.ac.cn*

extensively studied due to the ease of preparation (Lu and Yan, 2004; Han et al., 2005; Luo et al., 2008). MISGMs are fabricated by a conventional sol-gel process and incorporation of the template molecules into rigid inorganic or inorganic-organic networks. After removal of the template, molecular cavities with distinct pore size, shape, or chemical functionality remain in the cross-linked host. These “molecularly designed cavities” show an affinity for the template molecule over other structurally related compounds. As a satisfactory solid sorbent, the material should have not only high affinity and selectivity but also good site accessibility to target molecules. A promising solution to this problem is the development of surface molecular imprinting (Dai et al., 1999). The materials with binding sites situated at the surface show many advantages including high selectivity, more accessible sites, fast mass transfer and binding kinetics (Yang et al., 2005; Fang et al., 2005).

In this article, we reported a new imprinted amino-functionalized silica gel sorbent with binding sites situated at the surface for selective removal and separation of 2,4-D.

## 1 Experimental

### 1.1 Reagents

Silica gel (80–120 mesh, Qingdao Ocean Chemical Co., China) was used as the support to prepare 2,4-D-imprinted functionalized sorbent. Tetraethoxysilicane (TEOS), 3-aminopropyltriethoxysilane (APTES) (Wuhan University Chemical Factory, China), 2,4-dichlorophenoxyacetic acid (2,4-D), 2, 4-dichlorophenylacetic acid (DPAC), 2, 4-dichlorophenol(2,4-DCP) (Linfeng Chemical Co., Shanghai, China), acetic acid (HAc) (Tianjin Chemical Co., China) were used in this study. Doubly deionized water (DDW, 18 M $\Omega$ /cm) obtained from a WaterPro water system (Labconco Corporation, MO, USA) was used throughout the experiments. The mobile phase used for high performance liquid chromatography (HPLC) experiments was a mixture of methanol (Concord Technology Co., Ltd., Tianjin, China) and water (V:V = 4:1), and was filtered through a 0.45- $\mu$ m filter prior to use. All reagents used were of at least analytical grade.

### 1.2 Instrumentation

Absorption spectra and optical densities of solutions were recorded using a UV-2401 Spectrophotometer (Shimadzu, Japan). The chromatographic system consisted of a Model 600 HPLC pump and a Waters 2996 Photodiode Array Detector (Waters, Milford, USA). All separations were achieved on an analytical reversed-phase column (Symmetry-C18, 5  $\mu$ m, 4.6 mm i.d.  $\times$  25 cm length, Waters, USA) at a mobile flow rate of 1.0 mL/min under isocratic conditions at room temperature. The FT-IR spectra (4000–400  $\text{cm}^{-1}$ ) in KBr were recorded using a Magna-560 spectrometer (Nicolet, USA). The specific surface area and pore size distributions of the materials were measured by nitrogen adsorption/desorption at 77 K

using BET method by surface area and pore size analyzer (Gemini V 2380, Micromeritics, USA).

### 1.3 Preparation of 2,4-D-imprinted amino-functionalized silica gel sorbent

To activate the silica gel surfaces, 8 g of silica gel was mixed with 60 mL of 33% methanesulfonic acid and refluxed under stirring for 8 hr. The solid product was recovered by filtration, washed with DDW to neutral, and dried under vacuum at 70°C for 8 hr. To prepare the 2,4-D-imprinted amino-functionalized silica gel sorbent, 1 g of 2,4-D was dissolved in 5 mL of ethanol, and mixed with 2 mL of APTES. The mixture was stirred for 20 min, then 4 mL of TEOS was added. After stirring for 5 min, 1 g of activated silica gel and 1 mL of 1 mol/L HAc (as catalyst) were added. The mixture began to co-hydrolyzed and co-condensed after stirring for a few minutes, then incubated for 10 hr at room temperature. The product was filtrated and dried in a vacuum oven at 100°C for 8 hr. Thus, the activated silica gel surface was grafted with the complex. The sorbent was extracted with ethanol and 6 mol/L HCl under stirring for 2 hr to remove 2,4-D (Fig. 1). The product was isolated by filtration, washed with the mixture of ethanol and 1 mol/L HCl (V:V = 1:1), neutralized with 0.1 mol/L NaOH, and then washed with pure water. Finally, the sorbent was dried under vacuum at 80°C for 12 hr. For comparison, the non-imprinted functionalized silica gel sorbent was also prepared using an identical procedure, but without the addition of 2,4-D.

### 1.4 Adsorption test

To test the effect of pH, 20 mg of 2,4-D-imprinted sorbents were equilibrated with 10 mL solutions containing

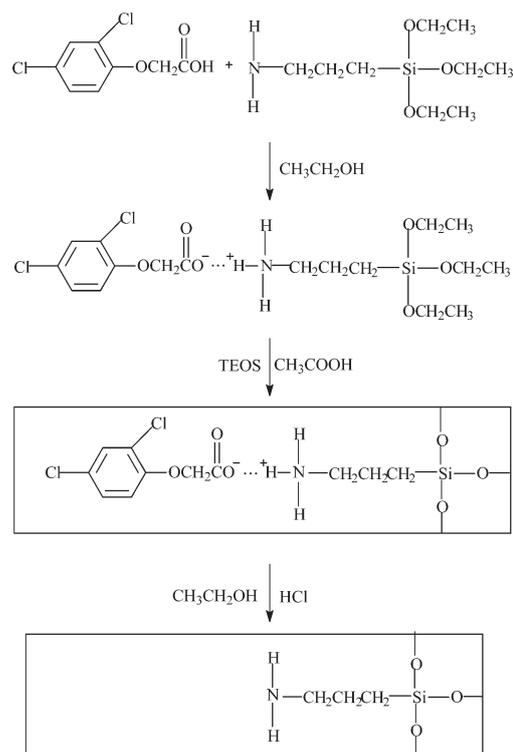


Fig. 1 Schematic synthesis route of 2,4-D molecular imprinted material.

200 mg/L of 2,4-D with different pH values from 1.00 to 7.50.

To measure adsorption capacity, 20 mg of 2,4-D-imprinted or non-imprinted sorbents were equilibrated with 10 mL of various concentrations of 2,4-D solutions with optimum pH. The mixtures were mechanically shaken for 1 hr at room temperature and separated by centrifugation. The supernatants were measured for the unextracted 2,4-D by UV spectrometry. Adsorption and competitive recognition studies were performed with the mixture solution of 2,4-D and structurally related compound 2,4-DCP or DPAC at the 200 mg/L level by HPLC.

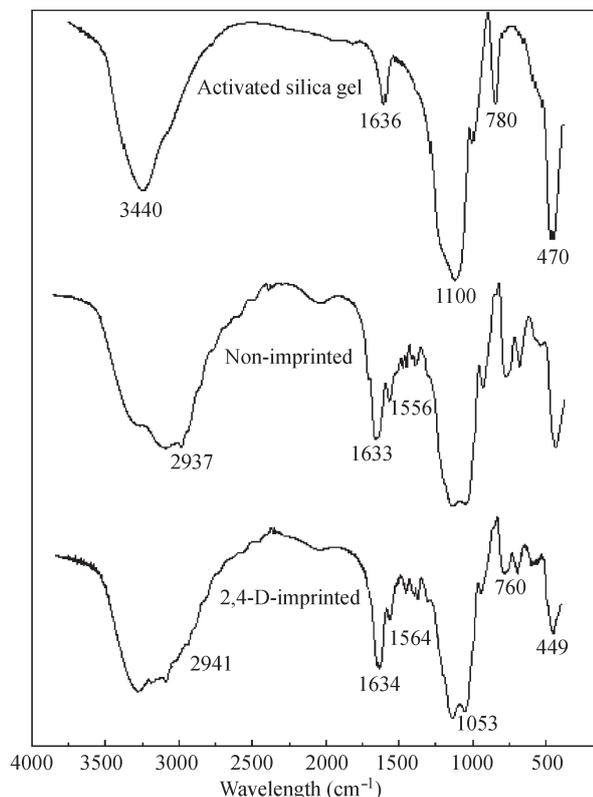
Uptake kinetics of 2,4-D by the imprinted functionalized silica gel sorbent was also examined. Sorbent 20 mg was added to 10 mL of 200 mg/L of 2,4-D solution. The mixture was mechanically shaken for 5, 10, 30, 60, 90 and 120 min at room temperature, respectively, then separated by centrifugation. The supernatants were measured for the unextracted 2,4-D by UV spectrometry.

## 2 Results and discussion

### 2.1 Characterization

To ascertain the presence of APTES in the functionalized silica gel sorbents, the FT-IR spectra for activated silica gel, 2,4-D-imprinted and non-imprinted amino functionalized silica gel sorbents are compared in Fig. 2.

The observed features around  $1100\text{ cm}^{-1}$  and  $976\text{ cm}^{-1}$  indicate Si–O–Si and Si–O–H stretching vibrations, respectively. OH vibration was reflected at 3440 and  $1636\text{ cm}^{-1}$ . The bands around 780 and  $470\text{ cm}^{-1}$  resulted from



**Fig. 2** FT-IR spectra of activated silica gel, 2,4-D imprinted, and non-imprinted sorbent.

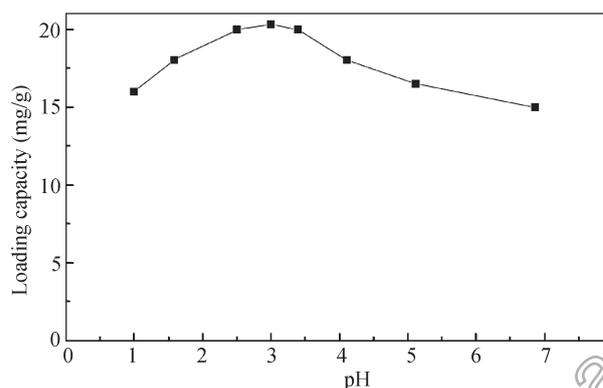
Si–O vibrations. A characteristic feature of the imprinted and non-imprinted sorbents when compared with activated silica gel is N–H bond around  $1560\text{ cm}^{-1}$ , C–H bond around  $2937\text{ cm}^{-1}$  and C–C stretching vibrations around  $1400\text{--}1500\text{ cm}^{-1}$ . These results suggest that  $\text{--NH}_2$  group was grafted onto the surface of activated silica gel after modification. Imprinted and non-imprinted sorbent showed similar location and appearance of the major bands. The imprinted sorbent has surface area of  $185\text{ m}^2/\text{g}$  with an average pore size of 8.9 nm while the activated silica gel has surface area of  $355\text{ m}^2/\text{g}$  with an average pore size of 8.6 nm.

### 2.2 Evaluation of adsorption

2,4-D ( $\text{p}K_a = 2.98$ ) can exist in solution in the molecular and ionized forms; therefore, one of the factors that influence its sorption is the pH of solutions. Figure 3 shows the binding of 2,4-D to polymers in different pH values from 1.00 to 7.50. The result shows that optimum pH range for the extraction of 2,4-D from aqueous solution was from 2.5 to 3.4. The pH value affects the ionic interaction between 2,4-D and sorbent. In strong acid solution,  $\text{--NH}_2$  group of the sorbent will be protonated, while in alkaline solution, 2,4-D will exist in the ionized forms, which does not benefit for adsorption. Therefore, in the following adsorption test, the pH of solution was adjusted to 3.0.

Figure 4 shows the effect of initial 2,4-D concentration on loading capacity of sorbents. Obviously, the binding capacity of the imprinted sorbent is larger than that of the non-imprinted sorbent.

Adsorption and competitive recognition studies were performed with 2,4-D and structurally related compound 2,4-DCP. Table 1 summarizes the data for uptake capacity, distribution coefficient ( $K_d$ ), selectivity coefficient of the sorbent ( $k$ ), and the relative selectivity coefficient ( $k'$ ) obtained in these competitive binding experiments. Comparison of the  $k$  values for the imprinted sorbent with the corresponding non-imprinted sorbent reveals a significant increase in  $k$  for 2,4-D through imprinting. The  $k$  (2,4-D)/2,4-DCP value of the imprinted sorbent (18.2) is 9.6-fold that of non-imprinted sorbent (1.9). The large  $k$  value of the imprinted sorbent is an indicative of its high selectivity for 2,4-D over the related compounds. This may result from the imprinting effect and the difference of the analytes' acidity. During the preparation of the imprinted

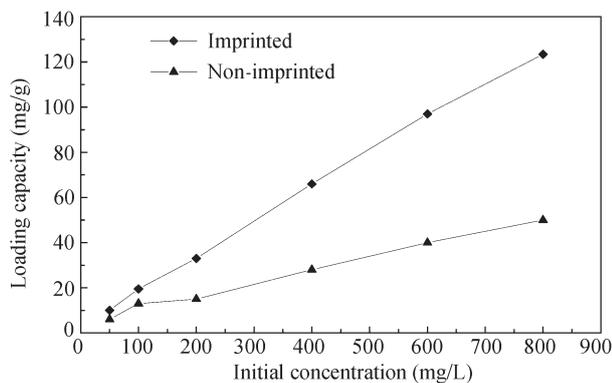


**Fig. 3** Effect of pH value on 2,4-D adsorption.

**Table 1** Competitive loading of 2,4-D and 2,4-DCP by the imprinted and non-imprinted sorbents

Sorbent	Initial solution (mg/L)		Capacity (mg/g)		$K_d$ (mL/g)		$k$	$k'$
	2,4-D	2,4-DCP	2,4-D	2,4-DCP	2,4-D	2,4-DCP	2,4-D/2,4-DCP	2,4-D/2,4-DCP
Imprinted	200	200	30.4	2.4	218	12	18.2	9.6
Non-imprinted	200	200	8.5	4.5	46	24	1.9	

$K_d$ : distribution coefficient,  $K_d = ((C_i - C_f)/C_f) \times V/m$ , where  $C_i$  and  $C_f$  represent the initial and final concentrations, respectively;  $V$  (mL) is volume of solution;  $m$  (g) is mass of gel;  $k$ : selectivity coefficient,  $k = K_{d1}/K_{d2}$ ;  $k'$ : relative selectivity coefficient,  $k' = k_{\text{imprinted}}/k_{\text{nonimprinted}}$ ; where,  $k_{\text{imprinted}}$  represents the selectivity coefficient of the molecular imprinted material and  $k_{\text{nonimprinted}}$  represents the selectivity coefficient of the nonimprinted material.

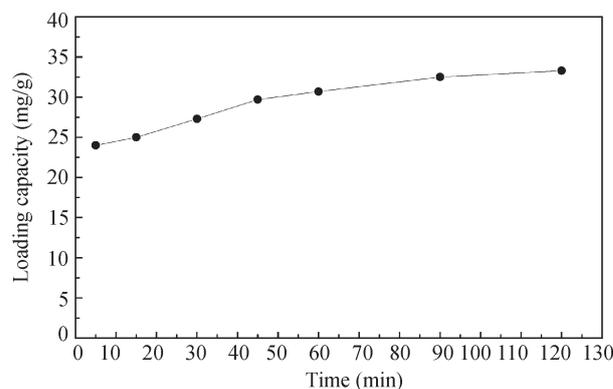
**Fig. 4** Effect of initial 2,4-D concentration on loading capacity of imprinted and non-imprinted sorbents.**Table 2** Comparison of the selectivity for 2,4-D with respect to DPAC with different materials

Compound	Loading capacity (mg/g)	Cross-reactivity
2,4-D	30.4 (100%)	100%
DPAC	5.1 (16.8%)	15%

Loading capacity of MISGMs prepared in this article with initial solution of 200 mg/L 2,4-D and 200 mg/L DPAC: numerical values in brackets refer to percentage of loading capacity against 2,4-D; cross-reactivity of the material prepared by Haupt et al. (1998) was calculated by dividing the  $IC_{50}$  value of 2,4-D by that of other compounds.  $IC_{50}$  values were obtained from the competition curves by nonlinear regression.

sorbent, the presence of 2,4-D made the  $-CH_2-CH_2-CH_2-NH_2$  chains arrange orderly. After the removal of 2,4-D, the imprinted cavities and specific binding sites of functional groups in a predetermined orientation was formed, whereas in non-imprinted sorbent the flexibility of  $-CH_2-CH_2-CH_2-$  which was joined to the  $-NH_2$  group resulted in no such specificity. On the other side, the acidity of 2,4-D ( $pK_a = 2.98$ ) is larger than that of 2,4-DCP ( $pK_a = 7.85$ ), thereby the interaction of 2,4-D with the  $-NH_2$  group is stronger than that of 2,4-DCP with the  $-NH_2$  group. Moreover, DPAC which is structurally more closely related to 2,4-D was selected as competitive compound at the same condition. The binding capacities of 2,4-D and DPAC are listed in Table 2 and compared with the similar study by Haupt et al. (1998). Although the criterion is different, they can still evaluate the selectivity on some extent. The results show that the prepared molecularly imprinted sol-gel materials have the merits of ease preparation and good selectivity.

Uptake kinetics of 2,4-D by the imprinted functionalized silica gel sorbent was also examined (Fig. 5). The results indicate that the imprinted sorbent has a fast uptake kinetics; 73% of binding capacity (200 mg/L 2,4-D onto

**Fig. 5** Kinetic loading for 200 mg/L 2,4-D onto 20 mg of imprinted sorbent.

20 mg imprinted sorbent) was obtained within 5 min. If the concentration of 2,4-D become lower, the time amount to saturation will be shorter. This means that the surface imprinting greatly facilitate the diffusion of the analyte to the binding sites.

### 2.3 Recycling of imprinted functionalized sorbent

In a test of sorbent recyclability, the imprinted functionalized sorbent was used to extract 2,4-D through five extraction/stripping cycles. The mixture solution of ethanol and 6 mol/L HCl ( $V:V = 1:1$ ) was used to strip the adsorbed 2,4-D, then the material was filtered and neutralized with 0.1 mol/L NaOH, and washed with pure water. The results are shown in Table 3.

The adsorption capacity of the sorbent in these five recycles was above 93% of that of the fresh sorbent which indicate that the prepared sorbent can be regenerated and used for many times on separation applications.

**Table 3** Extraction recyclability through five extraction/stripping cycles

Extraction cycle	1	2	3	4	5
Loading capacity (mg/g)	34.1	33.6	32.8	32.3	31.8
R (%)	100	98.5	96.2	94.7	93.2

R: ratio of the capacity of the sorbent in recycles against that of the fresh sorbent.

2,4-D-imprinted sorbent (100 mg) in 50 mL of 200 mg/L 2,4-D solutions at pH 3 were applied.

## 3 Conclusions

This work demonstrated the feasibility of the preparation of the molecularly-imprinted amino functionalized sorbent for selective removal of 2,4-D from aqueous

solution. The loading capacity and selectivity for 2,4-D of the imprinted sorbent is obviously larger than that of the non-imprinted sorbent. The sorbent possesses a fast kinetics for the extraction/stripping of 2,4-D and exhibits good recyclability.

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