

Electrospun Nanofibers Containing *p*-Nitrophenol Imprinted Nanoparticles for the Hydrolysis of Paraoxon*

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Abstract *p*-Nitrophenol imprinted nanoparticles with a size range of 150–300 nm in diameter were prepared through miniemulsion polymerization. The imprinted polymer exhibited higher adsorption capacity for *p*-nitrophenol than the non-imprinted polymer. The hydrolysis of paraoxon in aqueous phase can be accelerated in the presence of the *p*-nitrophenol imprinted nanoparticles. The hydrolysis rate of paraoxon incorporated with the imprinted nanoparticles was 2.83×10^{-7} mol/(L·min), which was about 3.7 times higher compared to the non-imprinted nanoparticles, 12.7 times higher to the spontaneous hydrolysis. The nanoparticles have been mixed with polyacrylonitrile solution and electrospun into nanofibers, which can also be used to accelerate the hydrolysis of paraoxon and conveniently separated from liquid phase for further processing.

Keywords: Molecular imprinting; Electrospinning; Nanofiber; 4-Nitrophenol; Paraoxon.

INTRODUCTION

Organophosphorous compounds, such as paraoxon (diethyl-4-nitrophenyl phosphate), parathion and malathion have been widely used as agricultural pesticides^[1]. The destruction of these nerve agents and organophosphorous pesticides has always been urgent and challenge in the world wide for their toxicity, carcinogenicity, bio-accumulation, etc.

A number of studies aimed at the destruction of organophosphorous compounds have been reported, including chemical degradation, biological oxidation, physical adsorption and so on^[2]. The use of natural enzymes should be the best choice for the degradation of organophosphorous compounds from the standpoint of safety and efficiency^[3]. However, the low stability and high cost have prevented the use of enzyme in large scale production and application.

A more economical and stable method has been developed, known as molecular imprinting technique (MIT)^[4] which offers a novel methodology to synthesize polymeric artificial catalyst^[5–8]. These enzyme mimics prepared using molecular imprinting technique have achieved relatively efficient destruction of organophosphate compounds^[9, 10]. By now, most of the molecularly imprinted catalysts for the destruction of organophosphorous compounds were prepared with the organophosphorous compounds^[11–13] or their transition state analogues^[14, 15] as the templates. These enzyme mimics were mainly focused on the catalytic efficiency of organophosphorous compounds, and the hydrolysis reaction rate has been accelerated obviously. However, the hydrolysis product

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(such as *p*-nitrophenol, the hydrolysis product of paraoxon) remains in the liquid medium system which is also environmentally harmful^[16]. So, the elimination of *p*-nitrophenol can be another aspect to be considered in the hydrolysis of paraoxon in addition to the catalytic efficiency.

In this work, molecularly imprinted nanoparticles were prepared with *p*-nitrophenol, the hydrolysis product of paraoxon, as the template, by miniemulsion polymerization. In order to realize convenient separation, the nanoparticles were then mixed with polyacrylonitrile solution and electrospun into nanofibers (the scheme as seen in Fig. 1). The molecularly imprinted polymers (MIP) are expected to act as adsorbing materials for *p*-nitrophenol and shift the hydrolysis equilibrium of paraoxon towards product formation. The hydrolysis test was preformed to confirm the effect of these *p*-nitrophenol imprinted polymers for the hydrolysis of paraoxon. Thus, the imprinted polymers are expected to not only accelerate the hydrolysis rate of paraoxon but also eliminate the environmental pollutant *p*-nitrophenol.

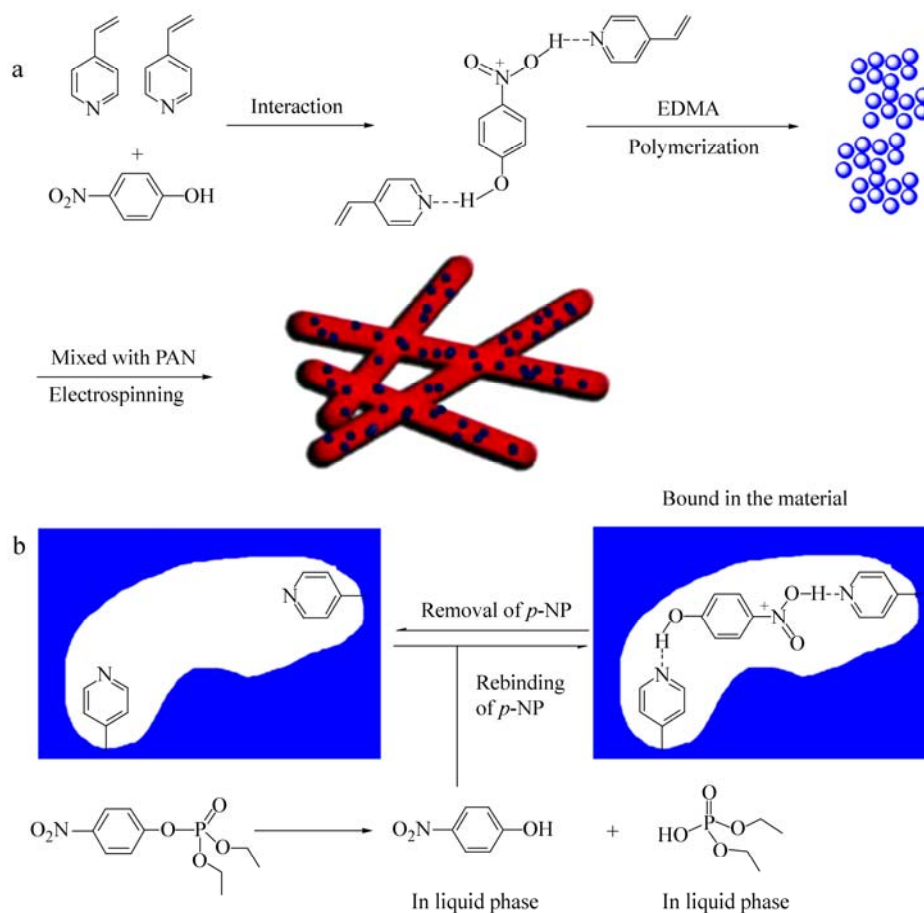


Fig. 1 Preparation process of the molecularly imprinted polymer particles and electrospun nanofibers (a) and the diagram of the hydrolysis of paraoxon (b)

EXPERIMENTAL

Materials

Paraoxon (standard substance, purity > 98%) was purchased from Shanghai Quandao Co. (China). Sodium dodecyl sulfate (SDS), hexadecane (HD), acrylonitrile (AN), ethylene glycol dimethacrylate (EDMA) and *p*-nitrophenol were all analytical grade and purchased from Tianjin Chem-reagent Institute (China). 4-Vinylpyridine (4-VP) was purchased from Alpha reagent Co. LTD. (USA). Azobisisoheptonitrile (ADVN) was purchased from J&K Chemical (China). EDMA and 4-VP were distilled in the presence of hydroquinone

inhibitor under vacuum and stored at 4 °C until use. All other chemicals were analytical grade and used as received.

Polyacrylonitrile was prepared in our laboratory by precipitation polymerization^[17]. The viscosity average molecular weight was 7.9×10^4 Da.

Characterization

UV-Vis spectra were recorded on a Shimadzu UV 2550 PC spectrophotometer (Suzhou, China). Ultrasonic Cell Disruptor, Sonics & Materials Inc. (USA), maximum power 400 Watts. Scanning electron microscope (SEM) images were taken with a Hitachi S-3500N (Japan) scanning electron microscope. Transmission electron microscope (TEM) images were taken with a FEI Tecnai G2 F20 electron microscope.

Preparation of *p*-Nitrophenol Imprinted Nanoparticles

p-Nitrophenol (0.1 mmol) and 4-VP (0.8 mmol) was dissolved in 300 μ L toluene, homogeneously mixed and incubated under 4 °C for 12 h. To this solution, EDMA (4 mmol), ADVN (0.01 g) and HD (100 μ L) were added to form the oil phase. Then, the oil phase was dropped into 20 mL deionized water containing 0.15 g SDS under magnetic stirring at 30 °C for 1 h. The mixture was sheared for 10 min (2 min $\times$ 5, interval 30 s) in ice water bath with the Ultrasonic Cell Disruptor to get a stable miniemulsion. The miniemulsion was finally transferred into a three-neck flask with a mechanical stirring at 220 r/min and purged with nitrogen gas for 30 min. The polymerization was performed at 55 °C for 22 h and then at 80 °C for 2 h under nitrogen gas protection. After polymerization, the resulted emulsion was broken with saturated solution of NaCl and centrifuged. The centrifugates were washed with water, ethanol, methanol/acetic acid (9/1, V/V) and ethanol, respectively. In order to confirm the *p*-nitrophenol was removed from the product, we detected the solution after washing using the UV spectrum at 400 nm till no *p*-nitrophenol was detected. The final polymers were dried in vacuum at 40 °C for 24 h. For comparison, non-imprinting nanoparticles (NIP) were prepared by the same procedure, only without *p*-nitrophenol in the polymerization process.

Electrospinning

The nanoparticles were first suspended in DMF and sonicated for 30 min. And the polyacrylonitrile was dissolved in DMF with a mechanical stirring. Then polyacrylonitrile solution was added to the nanoparticles suspension, and the mixture was stirred continually using a mechanical stirrer for at least 4 h. Electrospinning of nanofibers were carried out at 25 °C at a high voltage of 15 kV. The syringe used in the experiments had a capillary tip with a diameter of 0.7 mm. A copper wire was fixed to the capillary tip and used as the positive electrode. A grounded aluminum foil was used as the counter electrode and spread out at a distance of 20 cm from the capillary tip. Continuous polyacrylonitrile/imprinted nanoparticles nanofibers were collected on the aluminum foil in the form of a fibrous mat. After electrospinning, the nanofiber mats were placed in vacuum for at least 24 h to remove the residual organic solvent. After drying, the nanofibers were cut into strips before the following test.

Static Adsorption for *p*-Nitrophenol

In a typical static adsorption experiment, 30 mg nanoparticles were suspended in 4.9 mL of 20 mmol/L Tris-HCl buffer (pH = 9.0) by ultrasound. To this suspension, 100 μ L of 10 mmol/L *p*-nitrophenol in Tris-HCl buffer was added. Then the suspension was incubated at 30 °C in a water bath shaker. 300 μ L of the suspension was sampled and diluted with 2.7 mL Tris-HCl buffer (pH = 9.0) each hour. After centrifugation, the absorbance of the supernatant at 400 nm was determined using UV spectrophotometer.

The isothermal adsorption was performed in the same adsorption medium with the initial concentration of *p*-nitrophenol ranging from 0.2 mmol/L to 2.5 mmol/L and the amount of imprinted materials was 30 mg. The residual concentration of *p*-nitrophenol was detected after an incubation of 6 h.

The adsorption experiment of the nanofibers was performed under the same condition as the nanoparticles. Nanofibers without nanoparticles and pure nanoparticles were tested as control groups.

The amount of adsorbed *p*-nitrophenol per unit mass of the polymer ($\mu\text{mol/g}$) was calculated based on the formula, $Q = (c_{\text{total}} - c_{\text{residual}}) \times V/W$, where, c_{total} was the initial concentration of *p*-nitrophenol (mmol/L), c_{residual} was the concentration of *p*-nitrophenol detected by the UV spectrophotometer (mol/L). V was the volume of suspension (mL), and W is the weight of the polymer (g). The imprinting factor k ($k = Q_{\text{MIP}}/Q_{\text{NIP}}$) is defined as the adsorption quantity of imprinted polymers divided by the adsorption quantity of non-imprinted polymers.

Hydrolysis Activity for Paraoxon

In a typical hydrolysis experiment, 30 mg nanoparticles were suspended in 4.862 mL of 20 mmol/L Tris-HCl buffer ($\text{pH} = 9.0$) by ultrasound. To this suspension, 138 μL of paraoxon in acetonitrile (100 mg/10 mL) were added. The suspension was incubated at 30 $^{\circ}\text{C}$ in a water bath shaker. 300 μL of the suspension was sampled and diluted with 2.7 mL Tris-HCl buffer ($\text{pH} = 9.0$) each hour. After centrifugation, the absorbance of the supernatant at 276 nm was determined using an UV spectrophotometer. The hydrolysis test of nanofibers was performed under the same condition as the nanoparticles with the initial concentration of paraoxon of 1.0 mmol/L and the amount of the nanofibers is also 30 mg. Nanofibers without nanoparticles and pure nanoparticles were tested as control groups.

The hydrolysis degree of paraoxon was also calculated using the following equation: $\text{Hydrolysis (\%)} = (c_{\text{total}} - c_{\text{residual}})/c_{\text{total}} \times 100$, where, c_{total} was the initial concentration of paraoxon (mmol/L), c_{residual} was the concentration of paraoxon detected by the UV spectrophotometer (mmol/L). Hydrolysis (%) represented the percentage of paraoxon concentration changed.

RESULTS AND DISCUSSION

Synthesis of the Imprinted Nanoparticles

The 4-VP was chosen as the functional monomer because of the possible interaction with the *p*-nitrophenol such as the hydrogen bond, acid-base interaction and the π - π interaction^[18]. The morphologies of the prepared nanoparticles are shown in Fig. 2. The imprinted nanoparticles were spherical in shape with a size range of 150–300 nm in diameter.

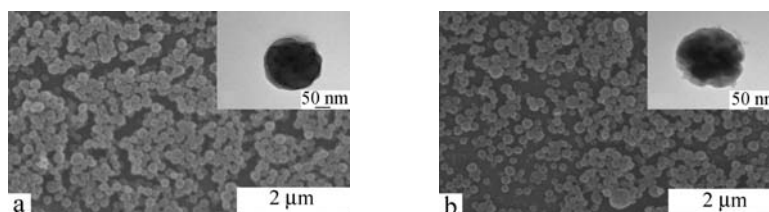


Fig. 2 SEM and TEM images of imprinted nanoparticles (a) and non-imprinted nanoparticles (b)

The infrared spectrum of the *p*-nitrophenol imprinted nanoparticles is showed in the Fig. 3. The absorption band at 2922 cm^{-1} was the stretching vibration of C—H bonds on methyl groups. Multiple peaks at 1600 cm^{-1} to 1450 cm^{-1} were responded to the aromatic ring which could be attributed to the pyridine ring of the 4-VP molecule. The absorption peak at 1729 cm^{-1} was the stretching vibration of C=O bonds on carbonyl groups. A minor absorption peak around 1640 cm^{-1} should be attributed to the stretching vibration of residual vinylic C=C bonds, which was possible a few of residual groups of the cross-linker EDMA in the polymers. These results indicated that the *p*-nitrophenol imprinted nanoparticles with 4-VP as the functional monomer have been obtained.

Electrospinning of the Nanofibers

The excellent weatherability and high resistance to chemical reagent of the polyacrylonitrile made it possible to be used in some hostile environment and ensured the stability of the composite nanofibers. Hence, polyacrylonitrile was chosen as the supporting material for the electrospun nanofibers containing *p*-nitrophenol imprinted nanoparticles.

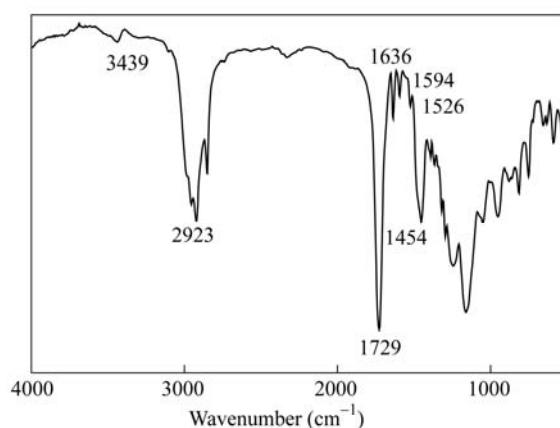


Fig. 3 IR spectrum of the imprinted nanoparticles

Polyacrylonitrile nanofibers containing different amounts of imprinted and non-imprinted nanoparticles were prepared with the same electrospinning condition. The morphological structures of these nanofibers were detected by SEM as shown in Fig. 4. As illustrated in the SEM images, pure polyacrylonitrile nanofibers showed a smooth surface and the diameter of the nanofiber was uniform and approximate 500 nm. When the nanoparticles were added to the spinning solution, the nanoparticles distributed in the surface of the nanofibers could be observed from the SEM image. At low nanoparticle content, most of the nanoparticles were independently distributed along the nanofibers. With the increase of the nanoparticle contents, the nanoparticles began to aggregate. Only when the nanoparticle content was less than 50 wt% (to the weight of nanofibers) the nanofibers could be electrospun normally, because of the more serious nanoparticle aggregation at higher nanoparticle contents^[19]. Additionally, the diameter of the nanofibers containing nanoparticles became uneven compared to the pure polyacrylonitrile nanofibers. This may be resulted from the damage in homogeneity of the spinning solution because of the adding of nanoparticles. And no obvious difference was found between molecular imprinted nanoparticles containing nanofibers (MF) and those of non-imprinted ones (NF).

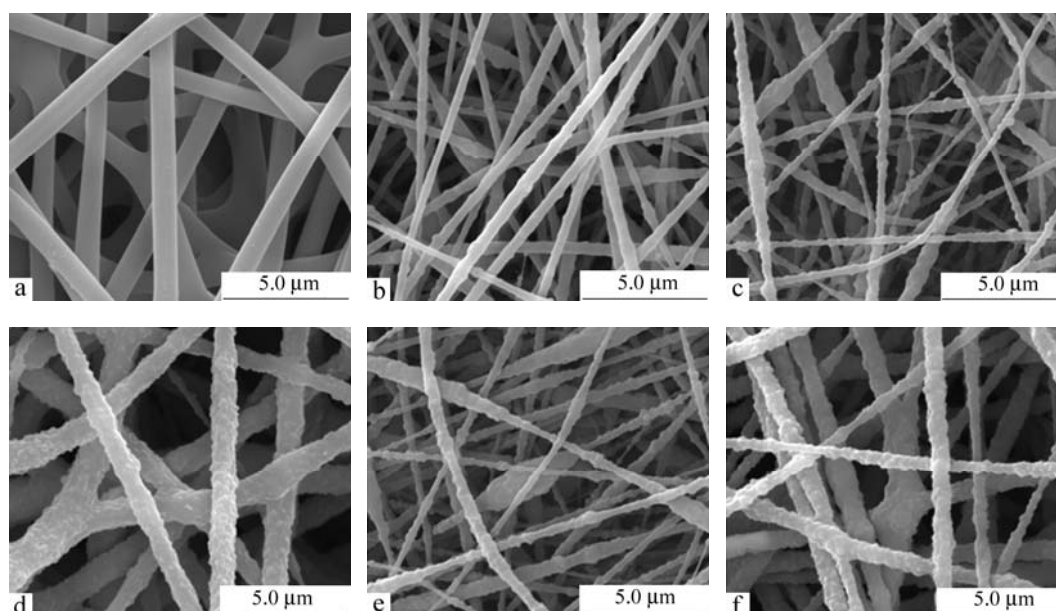


Fig. 4 SEM images of nanofibers with different nanoparticle contents: (a) 0 wt%, (b) 20 wt% MIP, (c) 33 wt% MIP, (d) 50 wt% MIP, (e) 33 wt% NIP and (f) 50 wt% NIP

Static Adsorption Behavior

Figure 5 shows the adsorption kinetics curves of the *p*-nitrophenol bound to the imprinted nanoparticles. It can be seen that the adsorption quantity has a rapid increase in 3 h, and then it increases slowly with the time extension till the adsorption equilibrium. A relevant graph of $\ln(c_0/c)$ versus time gives two linear plots within 4 h (shown in Fig. 5b). Obviously, the adsorption rate of the *p*-nitrophenol bound to the imprinted nanoparticles is higher than the non-imprinted ones and the imprinted nanoparticles present a larger equilibrium adsorption quantity. The imprinting sites in the nanoparticles make the penetration of *p*-nitrophenol easier, and larger adsorption quantity is also obtained through the specific adsorption cavities which can produce stronger binding with the templates.

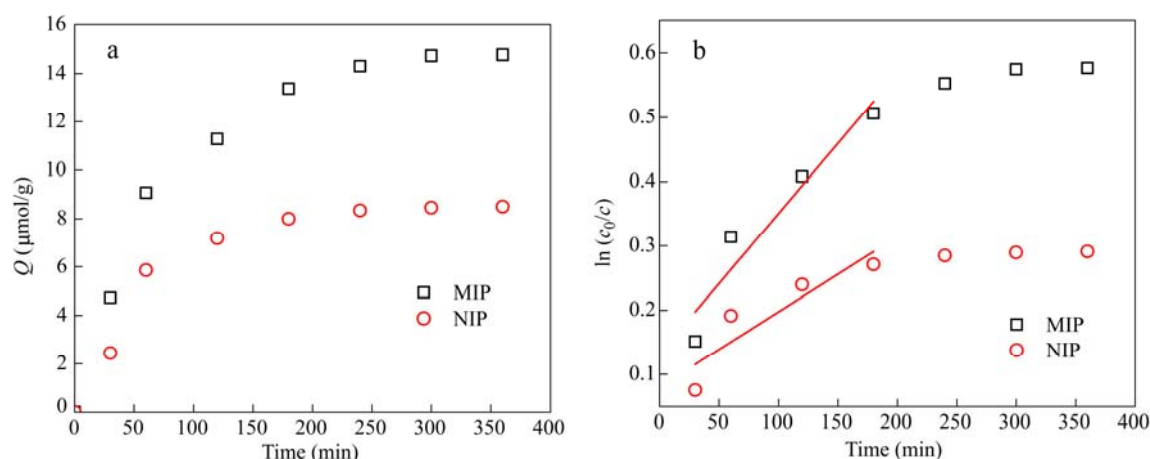


Fig. 5 Adsorption dynamic curve of *p*-nitrophenol for nanoparticles in Tris-HCl (20 mmol/L, pH = 9.0) ($c_{\text{initial}} = 0.2$ mmol/L; Polymer quantity: 6 mg/mL, 30 °C.)

The experimental equilibrium isotherms for adsorption of *p*-nitrophenol to the nanoparticles are shown in Fig. 6. As can be seen in Fig. 6(a), the adsorption capacities (Q) of *p*-nitrophenol increased with the initial concentration of the *p*-nitrophenol. And when the initial *p*-nitrophenol concentration was higher than 1 mmol/L, the adsorption capacities did not increase obviously. The adsorption capacities under the initial *p*-nitrophenol concentration of 1 mmol/L were observed to be 47.58 μmol/g for MIPs and 25.67 μmol/g for NIPs, and the imprinting factor was 1.85.

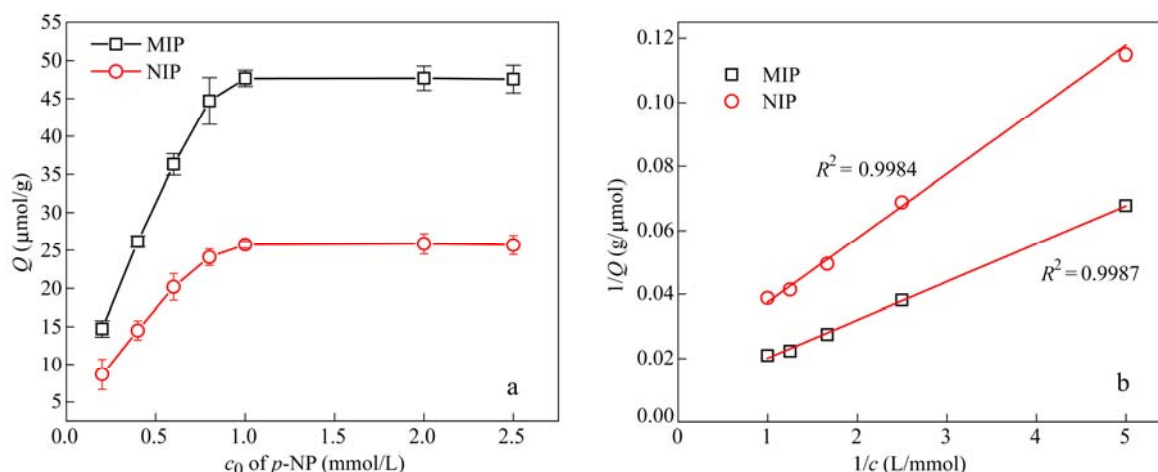


Fig. 6 Isothermal adsorption curve of *p*-nitrophenol (a) and Scatchard plot (b) (Tris-HCl (20mmol/L, pH = 9.0), $c_{\text{initial}} = 0.2$ –2.5 mmol/L; Polymer quantity: 6 mg/mL, 6 h, 30 °C)

When Langmuir adsorption isotherm was introduced to study the adsorption of *p*-nitrophenol by nanoparticles, the correlation coefficients were larger than 0.99. $Q/c = (Q_{\max} - Q)/K_d$ was one form of the Langmuir adsorption isotherm. Here, c is the initial concentration of *p*-nitrophenol (mmol/L), Q is the adsorption capacity of *p*-nitrophenol adsorbed per unit weight of polymers at equilibrium concentration ($\mu\text{mol/g}$), $Q_{\max}$ is the theoretical maximum adsorption capacity ($\mu\text{mol/g}$), K_d is the dissociation constants (mmol/L). Scatchard linearized plot of $1/Q$ versus $1/c$ was shown in Fig. 6(b). The theoretical maximum adsorption capacities ($Q_{\max}$) and dissociation constants (K_d) were found to be 121.65 $\mu\text{mol/g}$ and 0.012 mmol/L for imprinted nanoparticles, 57.24 $\mu\text{mol/g}$ and 0.020 mmol/L for non-imprinted ones, respectively. This demonstrates that the imprinting of *p*-nitrophenol has offered the stronger interaction between the nanoparticles and the template. Thus, the imprinted nanoparticles have shown larger adsorption ability than the non-imprinted ones (Fig. 6a).

Molecularly imprinted nanoparticles have shown fast binding kinetics and high target binding capacities owing to the short diffusion distances and large specific surface area^[20]. But an inconvenience was the separation of the imprinted nanoparticles, which would take too much time and energy to reduce the undesirable lose of the nanoparticles. Thus electrospun polyacrylonitrile nanofibers containing nanoparticles were prepared. To investigate whether the imprinted binding sites of the nanoparticles in the nanofibers are still accessible for target recognition, adsorption tests were performed with the composite nanofibers.

The effect of electrospinning on the imprinting effect of the nanoparticles was decided by the imprinting factor. After deducting the adsorption amount of polyacrylonitrile, which was 4 $\mu\text{mol/g}$, the imprinting factor of the nanoparticles in the nanofibers was calculated. The imprinting factor (k) was 1.67 (initial *p*-nitrophenol concentration was 1 mmol/L), which declined only by 9.8% compared to the pure nanoparticles. It indicates that the imprinted binding sites in the nanofibers remained accessible for *p*-nitrophenol and the imprinting effect was mainly preserved after the electrospinning process.

The adsorption of *p*-nitrophenol bound to the nanofibers with different nanoparticle contents is shown in Fig. 7. The adsorption capacity increases with the increase of the nanoparticle content. At low nanoparticle contents, the amount of *p*-nitrophenol bound to nanoparticles was small and the adsorption to the polyacrylonitrile could not be ignored, the difference between fibers containing imprinted and non-imprinted polymers was not obvious. Along with the increase of the content of nanoparticles in fibers, the effect of nanoparticles in the whole adsorption process was increased obviously.

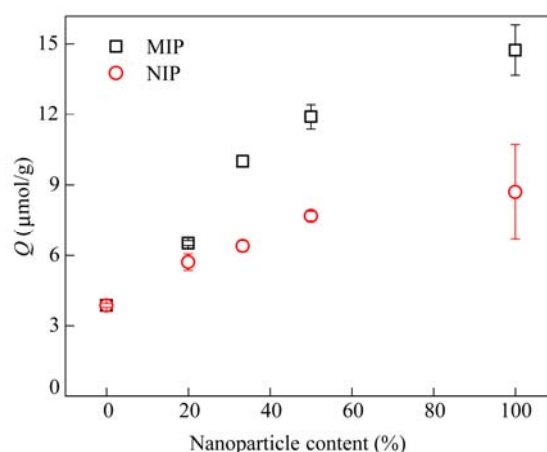


Fig. 7 Adsorption curve of *p*-nitrophenol for nanofibers (Tris-HCl (20 mmol/L, pH = 9.0), $c_{\text{initial}} = 0.2$ mmol/L; Polymer quantity: 6 mg/mL, 6 h, 30 °C)

Hydrolytic Activity

Figure 8 shows the time course of the paraoxon hydrolysis in the presence of nanoparticles. A sharp rising of these curves observed at the beginning represents the concentration decline of paraoxon, which could be

attributed to the adsorption of the nanoparticles. And the adsorption would get a balance within 30 min. Then these curves showed linear increase with the time no matter it was detected in the presence of the imprinted or the non-imprinted nanoparticles. But the paraoxon hydrolyzed in the presence of imprinted nanoparticles was faster than that in the presence of non-imprinted nanoparticles. The hydrolysis rate of paraoxon was 2.83×10^{-7} mol/(L·min) in the presence of imprinted nanoparticles, 7.60×10^{-8} mol/(L·min) for non-imprinted nanoparticles and 2.23×10^{-8} mol/(L·min) for spontaneous hydrolysis.

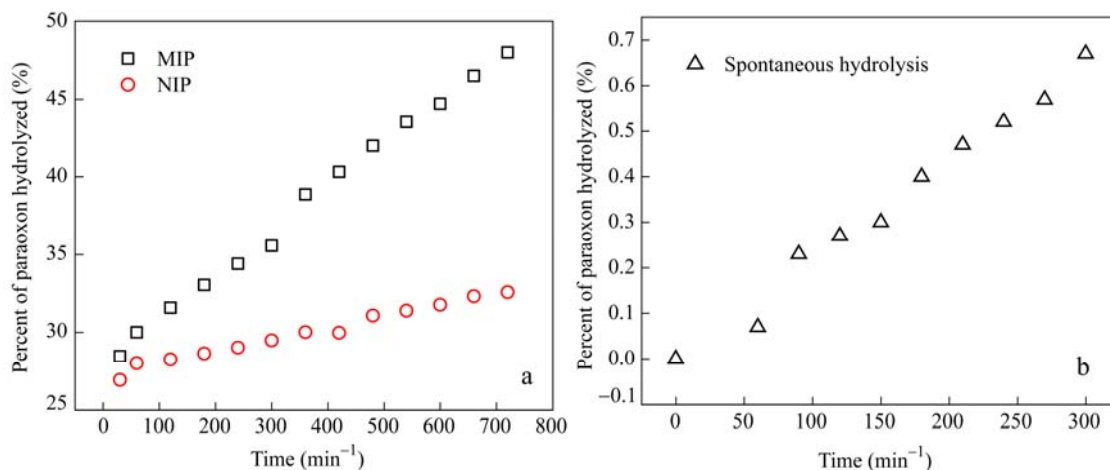


Fig. 8 Paraoxon hydrolysis with nanoparticles (a) and spontaneous hydrolysis (b) (Tris-HCl (20 mmol/L, pH = 9.0), $c_{\text{initial}} = 1.0$ mmol/L; Polymer quantity: 6 mg/mL, 30 °C)

Different from enzyme-catalyzed reactions which generally proceed by substrate recognition followed by the reaction, the hydrolysis of paraoxon here may come from three parts. The first part is the spontaneous hydrolysis of paraoxon shown in Fig. 8(b). The second part comes from the direct catalytic effect of the polymer, which can be expressed as the hydrolysis with the non-imprinted polymers which is 3.4-fold higher than the spontaneous hydrolysis. And the last part is the indirectly promotion resulting from the adsorption of *p*-nitrophenol to the imprinted nanoparticles, which would decrease the concentration of *p*-nitrophenol produced from paraoxon hydrolysis and promote the hydrolysis reaction to move to the positive direction (Fig. 1). It comes out that the presence of imprinted nanoparticles can increase the hydrolysis rate of paraoxon by 3.7-fold to the presence of non-imprinted nanoparticles, and 12.7-fold to the spontaneous hydrolysis.

The *p*-nitrophenol left in the medium was also detected after paraoxon hydrolysis of 24 h. The concentration of *p*-nitrophenol in the presence of imprinted nanoparticles was 1.31×10^{-4} mol/L, which was only about 16.7% to the theoretical concentration produced by the hydrolysis of paraoxon. Thus, the imprinted polymers prepared in this work can both accelerate the hydrolysis of paraoxon and eliminate mostly the hydrolysis product *p*-nitrophenol.

The Michaelis-Menten enzyme kinetic model was used to study the hydrolysis behavior of paraoxon in the presence of the imprinted nanoparticles (Fig. 9). To obtain the Michaelis-Menten constant of the molecularly imprinted nanoparticles, the initial reaction rates of hydrolysis were determined under different concentrations of paraoxon (0.2 mmol/L, 0.3 mmol/L, 0.5 mmol/L, 1 mmol/L and 2 mmol/L, Fig. 10a). In the Michaelis-Menten kinetics equation, $K = V_m \times S / (K_m + S)$, where, K is the initial reaction rate (mol/(L·min)), V_m is the maximum initial rate of the reaction (mol/(L·min)), S is the concentration of substrate (mol/L), and K_m is the Michaelis-Menten constant (mol/L), which reflects the affinity of an enzyme for a particular substrate (the lower the value of K_m , the higher the affinity). And $1/K$ versus $1/S$ was plotted which is called a Lineweaver-Burk plot (shown in Fig. 9b), $1/K = (K_m/V_m) \times (1/S) + 1/V_m$. After calculation, the value of V_m was 3.23×10^{-7} mol/(L·min) and K_m was 1.40×10^{-4} mol/L. The value of K_m was just as low as other traditional catalysts which ranges from 1.28×10^{-3} mol/L to 2.5×10^{-4} mol/L^[11].

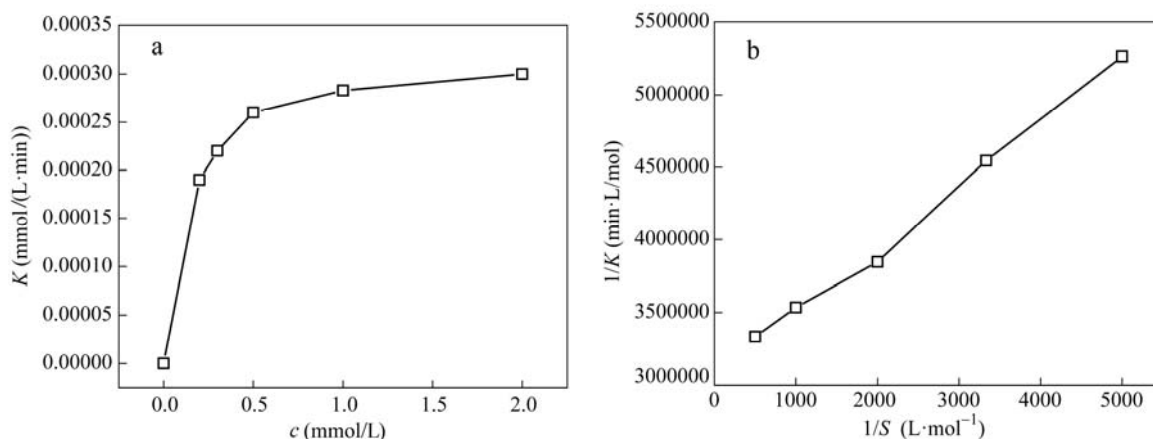


Fig. 9 The initial reaction rates (K) of hydrolysis (a) and Lineweaver-Burk plot of kinetic data of hydrolysis for paraoxon (b) (Tris-HCl (20 mmol/L, pH = 9.0), $c_{\text{initial}} = 0.2\text{--}2.0$ mmol/L; Polymer quantity: 6 mg/mL, 30 °C)

Compared to the traditional molecularly imprinted catalysts^[11–13] where the hydrolysis rate enhancements by a factor of dozens of times compared to the rate in non-catalyzed media that contains only buffer, in our study the enhancement was 12.7-fold which was just a medium value. But the residual *p*-nitrophenol was much less than the traditional molecularly imprinted catalysts.

The hydrolysis of paraoxon with nanofibers is shown in Fig. 10. The concentration of paraoxon in the hydrolysis medium changed just 10% with pure polyacrylonitrile nanofibers which was just a little more than the self-hydrolysis of paraoxon. The hydrolysis of paraoxon in the medium increases with the increases of the nanoparticle content in the nanofibers.

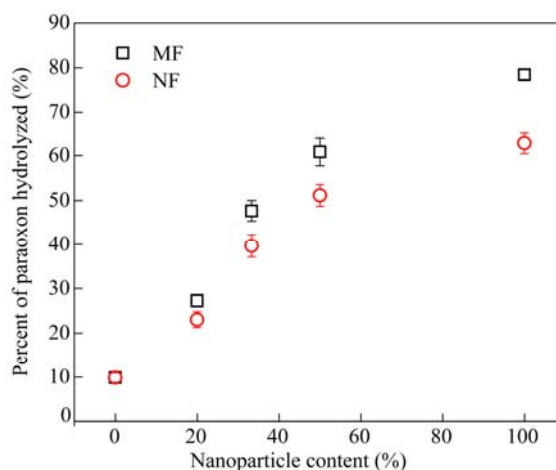


Fig. 10 Paraoxon hydrolysis with nanofibers (Tris-HCl (20 mmol/L, pH = 9.0), $c_{\text{initial}} = 1.0$ mmol/L; Polymer quantity: 6 mg/mL, 24 h, 30 °C)

CONCLUSIONS

We have prepared a kind of molecularly imprinted nanoparticles with the hydrolysis product of paraoxon, *p*-nitrophenol, as template. The imprinted nanoparticles exhibited higher adsorption capacity for *p*-nitrophenol than non-imprinted ones. The hydrolysis of paraoxon can be accelerated in the presence of the imprinted polymer. The hydrolysis rate of paraoxon in the presence of the imprinted nanoparticles was 2.83×10^{-7} mol/(L·min), which was 3.7 times higher compared to the non-imprinted nanoparticles, 12.7 times higher to the

spontaneous hydrolysis, while the concentration of *p*-nitrophenol left in the hydrolysis medium after 24 h is only 1.31×10^{-4} mol/L. The nanoparticles can be mixed with polyacrylonitrile solution and electrospun into nanofibers. The imprinting effect was mainly preserved after the introduction of electrospinning process.

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