Preparation and Characterization of Nonylphenol Magnetic Molecularly Imprinted Polymer

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Summary: Nonylphenol (NP) is a toxic xenobiotic compound classified as an endocrine disrupter, which can interfere with the hormonal system of numerous organisms, and then cause a series of pathological changes. It is of great significance to remove nonyl phenol from the environment. In this paper, an effective method for the preparation of molecularly imprinted nanoparticles was reported. Firstly, $Fe_3O_4@SiO_2$ magnetic carrier material modified by trimethoxysilane was achieved through three-step reaction. After that, the selective magnetic molecularly imprinted polymer sorbent for NP ($Fe_3O_4@SiO_2$-MIP) was synthesized by surface molecular imprinting technique, using NP as template, 4-vinyl pyridine (4-Vpy) as functional monomers, ethylene glycol dimethacrylate (EGDMA) as crosslinker and azobisisobutyronitrile (AIBN) as initiator. The morphous, composition, structure and performance of the polymer adsorbent was characterized by SEM, TEM, FT-IR, XRD, EDS, VSM and nitrogen adsorption-desorption techniques. The results indicated that the polymer adsorbent was successfully prepared. The size of the polymer particle was about 50 nm, the aperture on the surface was 3.71 nm, the BET specific surface area was 61.80 m^2/g and the Langmuir specific surface area was 101.24 m^2/g. The selective adsorption rate for NP of 0.5 mmol/L attained value of 86.5%, and for NP with low concentration (less than 2.0 mg/L), the selective adsorption rate reached more than 90%. The synthesized magnetic molecularly imprinted polymer had higher selective recognition ability towards the template molecule nonylphenol. It has good magnetism and can be rapidly separated after being employed by using adscititious magnetic field. It has potential application value in treatment and enrichment of nonylphenol.

Introduction

Nonylphenol (NP) is a major raw material and intermediate for fine chemical industry, which was commonly used in industrial production and agricultural activities as surfactant, antioxidant, lubricant additive, printing and dyeing auxiliary, emulsifier, modifier and stabilizer, and so on [1]. Its production and consumption has been increased year by year. As a result, the problem of environment is becoming more and more serious, posing a serious threat to human health.

In 1984, Giger [2] and his co-researchers from Switzerland established that nonylphenol is able to interfere with the secretion of estradiol hormone of organism endocrine system, lead to human endocrine system disorders and cause a series of pathological changes, and was known as *sperm killer*[3]. NP is classified as priority and persistent contaminants due to its relatively high toxicity and a long period of endanger incubation. Even if it′s concentration is very low in the aquatic environment, it is very harmful.

NP and NPE were classified as the substances prohibited to import and export in *the Directory of China Strictly Limit Import and Export of Toxic Chemicals* released in early 2011. According to the standard recommended by the US Environmental Protection Agency (U.S. EPA), In fresh and salt water, the concentration of NP should not exceed 6.6 μg/L and 1.7 μg/L, respectively[4]. At present, the nonylphenol pollution control has been imminent. It is generally difficult to separate and detect NP from the mixture of common concomitant disrupting compounds BPA and OP and so forth. Simultaneously, there also exists defects in low separation efficiency and analyte loss easily. Therefore, selective extraction and sensitive recognition of target NP from aqueous samples, especially drinking water is frequently required. In this regard, it is of great significance to synthesize a material with high selectivity and large adsorption capacity for clean-up and enrichment of NP.

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Molecular imprinting technique is a well-established and simple technology developed in recent years, which has been widely used in many areas, such as biological purification, enrichment, separation and detection and so forth. Molecularly imprinted polymers (MIPs) are a new kind of polymer biomimetic materials with desired predetermination, specific selectivity and wide practicability [5].

Nowadays, MIPs are commonly prepared by traditional methods, for example, bulk polymerization, the polymers prepared by these methods need grinding and sieving before being employed, the grinding and sieving process is time-consuming and laborious, the adsorption binding sites lose much more in the grinding process, and the obtained particles are irregular in size and shape, these all cause low rebinding capacity and poor site accessibility to target. In addition, because of the polymers′ highly cross-linked structure, it is more difficult for the template molecule inside the polymers to be eluted [6].

To resolve these problems, numerous efforts have been focused on exploring a method combined magnetic separation and surface molecular imprinting technique to prepare magnetic composites using Fe_3O_4 as carrier.

The MMIPs have been expected as an alternative surface imprinted support material due to their intriguing nanoscale dimensions, high specific surface area, mechanical strength and chemical stability. Thus, most recognition sites were situated at the surface of the imprinted complicated materials, which is easy to be bound with template molecule. So the adsorption capacity of the imprinted adsorbent can be effectively increased and the time required to reach adsorption equilibrium can also be reduced. The adsorption efficiency will be increased, and these are favorable for elution and re-binding of the target molecule [7, 8]. When Fe_3O_4 are encapsulated into MIPs, the MMIPs will not only improved specific selective adsorption capacity of the target pollutants from complex matrix compared with traditional imprinted polymer, but also be easily collected and separated by an external magnetic field without additional centrifugation, filtration and membrane separation because of their significant magnetic susceptibility, which greatly increase the adsorption rate and recycling efficiency of them.

In the present research, magnetic separation

technology was combined with surface molecularly imprinting technique to prepare NP magnetic molecularly imprinted polymer nanocomposites. The physical and chemical properties and the specific selective recognition capabilities of the imprinted polymer nanocomposites were characterized. The aim of the present work was to provide a new way for the efficient and rapid removal of NP from complex matrices.

Experimental

Materials and Reagents

Ferric trichloride ($FeCl_3·6H_2O$), ferrous chloride ($FeCl_2·4H_2O$), tetraethyl orthosilicate (TEOS), Silane, ethenyltrimethoxy (A-171) were purchased from Sinopharm Chemical Reagent Co., Ltd.; Poly (4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA) was obtained from Sahn Chemical Technology Co., Ltd. Shanghai China.；Nonyl phenol (NP), 4-vinyl pyridine (4-vpy), Ethylene glycol dimethacrylate (EGDMA), Azobisisobutyronitrile (AIBN), Phenol, Bisphenol A (BPA), Octyl phenol (OP) were all obtained from Shanghai Jingchun Biological Technology Co., Ltd.

Preparation of Magnetic Molecularly Imprinted Polymers

Preparation of Fe_3O_4 Magnetite: Nano-Fe_3O_4 was prepared by chemical co-precipitation method[9, 10]. 4.97 g of ferrous chloride and 10.14 g of ferric trichloride were dissolved in 50 mL of deionized water in 500 mL three-necked flask, the mixture was mechanically stirred vigorously at 70 ▯ until the iron salts added in were fully dissolved, and then 100 mL of sodium hydroxide solution (5 mol/L) was added into the mixture drop by drop with a constant pressure burette, soon after, 2 g of Poly (4-styrenesulfonic acid-co-maleic acid) sodium salt was dispersed into the mixture, next, the mixture was stirred for 30 min and cooled down to room temperature, the black precipitate was separated by putting the vessel on permanent magnet, and washed several times with deionized water, so the nano-Fe_3O_4 obtained by vacuum dehydration at 60 ▯ for 24 h.

Preparation of $Fe_3O_4@SiO_2$ Microspheres: $Fe_3O_4@SiO_2$ was prepared using Stöber method [11]. Fe_3O_4 (2 g), ammonia (8 mL 25 wt%), deionized water (40 mL) and isopropyl alcohol (140 mL) were mixed in a 500 mL flask, 1 mL tetraethyl

orthosilicate (TEOS) was dispersed into the mixture in ultrasonic bath for 10 min, and then the mixture was vigorously stirred for 10 h at room temperature. A stable suspension was obtained, the black magnetic precipitates were separated from the solvent with a permanent magnet and washed repeatedly with deionized water and ethanol by turns, until the pH of washings became neutral, the precipitate was then dried at 60 □ for 24 h.

Alkylation of $Fe_3O_4@SiO_2$: The preparation of alkylated $Fe_3O_4@SiO_2$ nanoparticles were carried out by mixing $Fe_3O_4@SiO_2$ (1.5 g) with anhydrous toluene (180 mL), soon after being stirred in ultrasonic bath for 10 min, then 12 mL of silane ethenyltrimethoxy (A-171) was added to the mixture, deoxidized under nitrogen gas atmosphere for 30 min. The reaction was kept at 80 □ with magnetic stirring for 24 h [12, 13]. The product was isolated by an external magnetic field, and then, washed 5 times with anhydrous toluene and anhydrous ethanol, respectively. The final alkylated $Fe_3O_4@SiO_2$ microspheres were dried in a vacuum drying oven at 40 □ for 24 h. So the -C=C bond was grafted on the surface of magnetic $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2$-C=C was obtained.

Synthesis of MMIP-NP: The preparation procedure of the MMIP-NP was as follows[14]. 1.0 mmol of NP and 1.0 mmol of 4-vyp were dissolved in 50 mL of toluene and the mixture was placed in refrigerator at 4 □ after ultrasonic dispersion, which was conducive to pre-assembly between template molecule and the functional monomer. Next, 1g of modified magnetic $Fe_3O_4@SiO_2$ particles, 2 mmol of ethyleneglycol dimethacrylate (crosslinker) and 10 mg of azobisisobutyronitrile (initiator) were added into the mixture by turns. Moreover, the mixture was dispersed in ultrasonic bath for 10 min, and bubbled with nitrogen to remove oxygen in the solution for 30 min. In a sealed container and under nitrogen protection, the reaction was allowed to proceed in a water bath with mechanical stirring at 65 □ for 24 h. After the polymerization, synthesized sorbents were handled by vacuum filtration and washed five times with copious of anhydrous methanol in an ultrasound bath to remove the remaining reactant and monomer self-polymer. The surface molecularly imprinted polymers obtained were transferred into a soxhlet extractor and washed with the mixed liquor of methanol/acetic acid (9:1, V/V) to remove the template molecules for 24 h, then washed repeatedly with anhydrous methanol in ultrasonic bath until the pH of washings became neutral, finally, the obtained

MMIPs were dried in a vacuum drying oven at 40 □ for 12 h.

In comparison, the magnetic non-imprinted polymers (MMIPs) were prepared as a blank in parallel, the preparation method is mainly same as that mentioned above, but no NP was added. The synthetic route was shown in Fig.1.
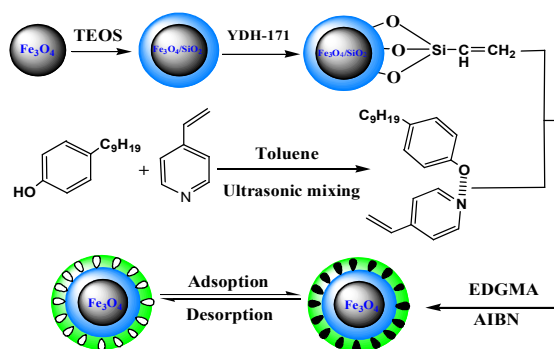
The Characterization of Imprinted Polymer

Fig. 1:   The schematic illustration of synthetic route for $Fe_3O_4@SiO_2$-MIP.

The materials were treated by spray-gold for 15 min and then observed by scanning/transmission electron microscope (SEM/TEM-10 Kv).

Fourier transform infrared spectroscopy was recorded on Spectrum 100 FT-IR instrument in the region between 4000 and 400 cm^{-1} using KBr disks.

Polycrystalline X-ray diffraction patterns were recorded to analyze the samples of Fe_3O_4, $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2$-C=C and $Fe_3O_4@SiO_2$-MIP by Rigaku D/max-γB X-ray diffract meter (XRD).

The specific surface area of $Fe_3O_4 @ SiO_2$-MIPs was obtained by nitrogen adsorption-desorption isotherms determined by Micromeritics ASAP-2020 V3.04 H instrument at 77.4 K.

The magnetic performance of microspheres Fe_3O_4 and $Fe_3O_4@SiO_2$-MIPs were determined using a VSM (7410 Lake Shore) under a magnetic field of -20000 Oe ~ 20000 Oe, and the test temperature was

300 K, the mass of sample was between 10 mg~30 mg.

Specific Selective Recognition Experiments

Selective adsorption is one of the most significant character of molecularly imprinted polymers, in order to estimate the selective recognition and high affinity between $Fe_3O_4@SiO_2$-MIPs and template molecule NP[15], in this work, structural analogs phenol, BPA and OP were chosen as competitive molecule to examine the selective recognition of the synthetic MMIPs to NP.

Experimental procedure: at first, a group of 30 mg of MMIPs ($Fe_3O_4@SiO_2$-MIP) or MNIPs ($Fe_3O_4@SiO_2$-NIP) were weighed accurately and added into centrifuge tubes, each of which contained 20 mL ethanol solution with 0.5 mmol/L of NP, phenol, BPA and OP, respectively. After binding experiments, the suspension was oscillated at room temperature for 2 h, then centrifuged the mixtures at the rate of 10000 rpm for 5 min, soon after, sampled the supernatant, and the absorbance of NP and structural analogs solutions were determined by a UV-vis spectrophotometer. Then, the concentration of NP, phenol, BPA and OP in supernatant can be calculated. And the removal rate η (%) of each substance could be calculated according to the variation of the concentration before and after adsorption.

Results and Discussion

Characterization and Analysis

Analysis of Fourier Transform Infrared (FTIR) Spectroscopy

Functional groups and chemical bonds of the test compound can be determined according to the position, intensity and shape of each peak in the infrared absorption spectrum. Fourier transform infrared spectra (FT-IR) of Fe_3O_4, $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2$-C=C and $Fe_3O_4@SiO_2$-MIPs are shown in Fig.2.

It can be seen from the spectrogram of Fe_3O_4 nanoparticles, the absorption band at 578 cm^{-1} corresponds to the stretching vibrations of Fe-O, which illustrated iron oxide was synthesized.

The characteristic absorption bands at 1541

cm^{-1} and 1620 cm^{-1} indicate that there may be exist the symmetric and asymmetric carboxylate group, derived from iron dispersant Poly (4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA) [10], indicating that PSSMA participated in synthesis of the product.
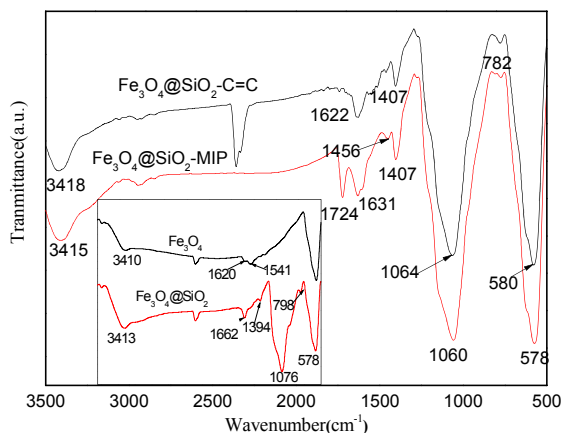

Fig. 2: FT-IR spectra of Fe_3O_4, $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2$-C=C and $Fe_3O_4@SiO_2$-MIP

Compared to the Fe_3O_4 nanoparticles, in the spectrum of $Fe_3O_4@SiO_2$, the absorption bands at 1076 cm^{-1} and 798 cm^{-1} corresponded to the O-Si-O stretching vibrations and Si-O vibration, respectively, indicating that SiO_2 layer were successfully coated on the surface of Fe_3O_4 [16]. The observed feature about 1394 cm^{-1} and 3414 cm^{-1} result from the -C-H, O-H which provided by tetraethylothosilicate and isopropanol.

As shown in spectrogram of $Fe_3O_4@SiO_2$-C=C, the presence of peaks at 1622 cm^{-1} and 2250 cm^{-1} were attributed to the stretching vibrations of C=C and =C-H from silane coupling agent A-171[17], indicating that the active -C=C bond was successfully grafted on the surface of magnetic $Fe_3O_4@SiO_2$, this is favorable for the synthesis of MIPs. Compared with $Fe_3O_4@SiO_2$, the peak at 798 cm^{-1}, 1076 cm^{-1} and 1394 cm^{-1} was shifted to 782 cm^{-1}, 1064 cm^{-1} and 1407 cm^{-1}, respectively. This change was originated from the reaction of coupling agent silane A-171 on the surface of magnetic $Fe_3O_4@SiO_2$

It was clearly observed in the spectrum of $Fe_3O_4@SiO_2$-MIP that a peak at 1060 cm^{-1} was assigned to the O-Si-O stretching vibrations. A new

absorption bands at 1724 cm^{-1} is due to the C=O stretching vibration, these attributed to the carbonyl group of EGDMA employed as crosslinking agent in the process of synthesis of MIPs [15], indicating that the polymerization process has been successful. The band at 1456 cm^{-1} is due to the C-N stretching vibration, it is related to the grafting of 4-Vpy. Compared with spectrogram of Fe$_3$O$_4$@SiO$_2$-C=C, the band at 1622 cm^{-1} was shifted to 1631 cm^{-1} and the peak at 2250 cm^{-1} was disappeared. This is because the group -C=CH$_2$ was involved in the polymerization.

The analysis given above indicates that NP magnetic molecularly imprinted polymer was prepared successfully.

SEM and TEM Observation

Fig. 3 shows the microscopic images of Fe$_3$O$_4$ (A) and Fe$_3$O$_4$@SiO$_2$-MIPs (B) examined by SEM and TEM.

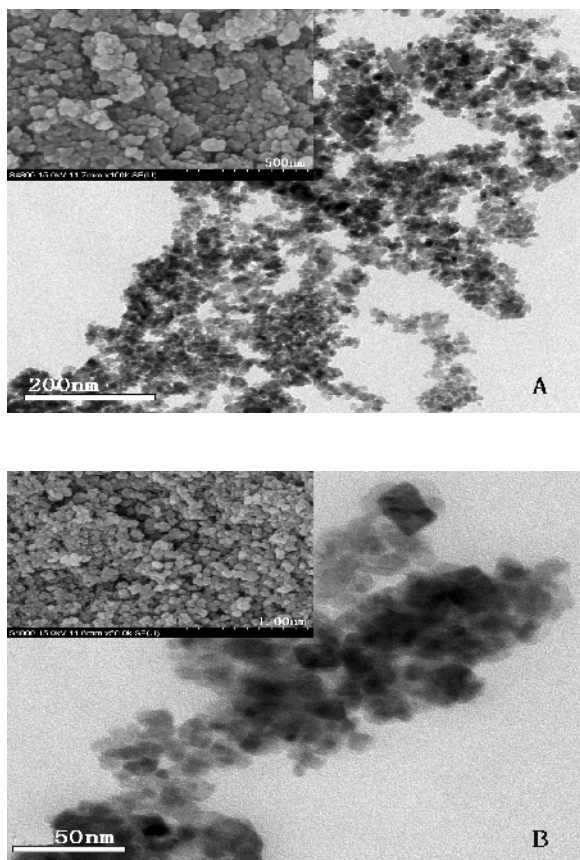Fig. 3: SEM/TEM micrograph of Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$-MIPs microspheres.

Fig. 3A showed that the surface of Fe$_3$O$_4$ particles prepared was smoothed and well-distributed, but there existed the particles agglomeration. The distribution of particle size was narrow, the diameters of Fe$_3$O$_4$ particles ranged from 30 nm to 40 nm. The size of the particles prepared by this work has been reduced and has a certain increase in dispersibility [10]. As can be observed in Fig. 3B, compared with Fe$_3$O$_4$ nanoparticles, the surface of the imprinted polymer particles was not enough smooth and the dispersibility of the particles was enhanced, this is because silica was used to encapsulate Fe$_3$O$_4$ nanoparticles to form the hydrophilic surface of Fe$_3$O$_4$@SiO$_2$ to prevent Fe$_3$O$_4$ nanoparticles from aggregation [18]. The particles of MMIPs synthesized were well-distributed and increased in size. The diameter of the particles ranged from 55 to 75 nm. The TEM images clearly show that there exist smudged polymer layer on the particle surface, and the thickness of the imprinting polymer layer is estimated to be about 20~30 nm with a relatively narrow size distribution, the polymer layer should be the product of SiO$_2$ layer formed by TEOS and co-polymerization of functional monomer 4-Vpy and cross-linking agent EGDMA [19].

Energy Dispersive Spectrum (EDS)

The Energy dispersive spectrum and the elements and atomic mass percentage content of Fe$_3$O$_4$@SiO$_2$ (A) and Fe$_3$O$_4$@SiO$_2$-MIP (B) were shown in Fig.4.

Reference standard substances selected for: O and Si referenced SiO$_2$, Fe element referenced Fe[9]. The peak of Fe and O element presented remarkably, while the peak of C and Si element were also obvious in both Fig. 4A and Fig. 4B. Fe element content of the analyte was the highest, proved that the main component in the materials measured was iron. Fig. 4 shows that silicon content of Fe$_3$O$_4$@SiO$_2$ sample was 6.12%, indicating that the SiO$_2$ layer was successfully coated on the surface of Fe$_3$O$_4$ by using TEOS. From Fig. 4B, we can see, silicon content of Fe$_3$O$_4$@SiO$_2$-MIP sample increased to14.17 %, this is because the C=C functional group was grafted on to the surface of Fe$_3$O$_4$@SiO$_2$ modified by A-171, and, at the same time, the silicon in A-171 was also grafted on the surface.

But Fe content of Fe$_3$O$_4$@SiO$_2$-MIP sample reduced 10%, which is consistent with the reduction of magnetism of the polymer adsorbent determined by VSM (see below) compared with that of carrier

material, further indicating that the polymer imprinting layer was finally synthesized on the surface of the carrier material and we have got the expected purpose.
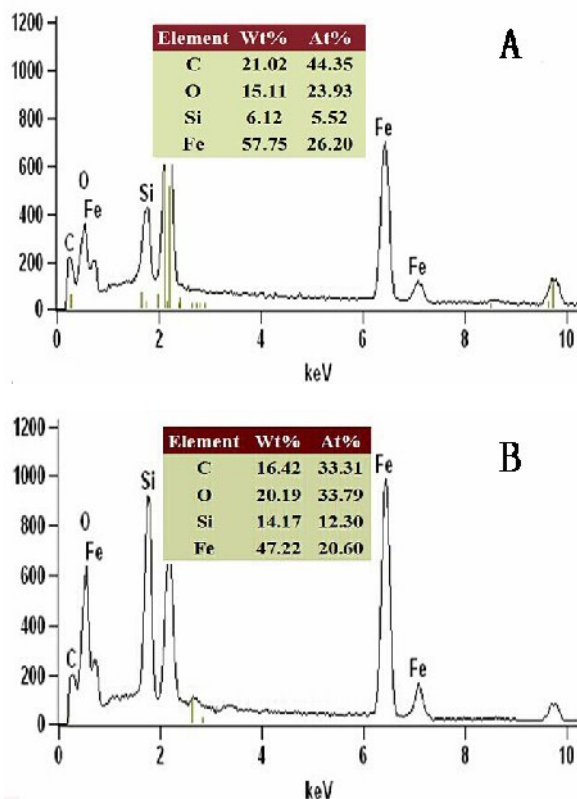

Fig. 4:   Energy dispersive spectrum of (A) $Fe_3O_4@SiO_2$ and (B) $Fe_3O_4@SiO_2$-MIP

X-ray Diffraction (XRD)

X-ray diffractograms for Fe_3O_4 (A), $Fe_3O_4@SiO_2$ (B), $Fe_3O_4@SiO_2$-C=C (C) and $Fe_3O_4@SiO_2$-MIPs (D) are shown in Fig. 5. From the XRD spectra of the Fe_3O_4 , $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2$-C=C and $Fe_3O_4@SiO_2$-MIPs samples shown in Fig. 5, we can see, there exist six characteristic diffraction peaks located at $2\theta= 30.43°$, $35.47°$, $43.19°$, $54.44°$, $57.27°$ and $62.89°$, revealing the presence of Fe_3O_4 crystal structure, and the peak positions could be indexed to (220), (311), (400), (422), (511) and (440) of crystalline Fe_3O_4, respectively, which match well with the database of magnetite in the JCPDS-International Center for Diffraction Data (JCPDS card: 19-629) [20]. This proves that the product obtained contains monophase

Fe_3O_4 crystal. The diffraction peaks of silicon and other substance did not appear in the XRD pattern, this conclusion conforms to the results reported in some literatures [21, 22].

Compared with curve A, it could be seen from curves B, C and D that the XRD patterns of $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2$-C=C and $Fe_3O_4@SiO_2$-MIP was similar to Fe_3O_4, indicating that they had the same cylinder wall structure and interplanner spacing. This shows that the crystal structure of carrier Fe_3O_4 did not change with the silica coating and alkylated modification and increase in thickness of polymer film.

With the increase in thickness of silica coating layer on the surface of Fe_3O_4, the shielding effect was reinforced, so the intensity of the peaks for $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2$-C=C, and even for $Fe_3O_4@SiO_2$-MIPs, decreased [23]. Such as the characteristic absorption peak (220) and (422) in curve C and D are very weak, they almost can not be seen. These results suggest that the Fe_3O_4 nanoparticles were really embedded into the core of nanoparticles.
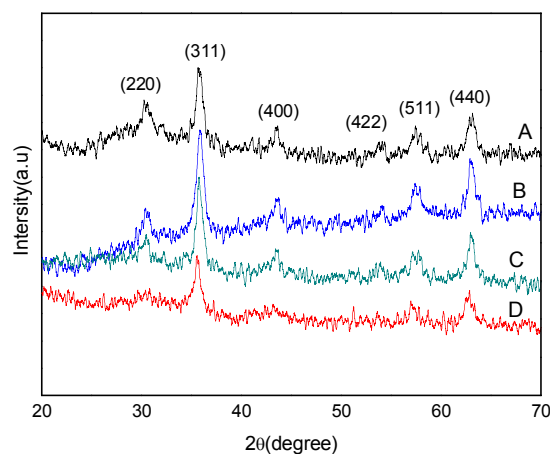

Fig. 5:   XRD patterns of (A) Fe_3O_4, (B) $Fe_3O_4@SiO_2$, (C) $Fe_3O_4@SiO_2$-C=C, and (D) $Fe_3O_4@SiO_2$-MIPs

Magnetic Performances

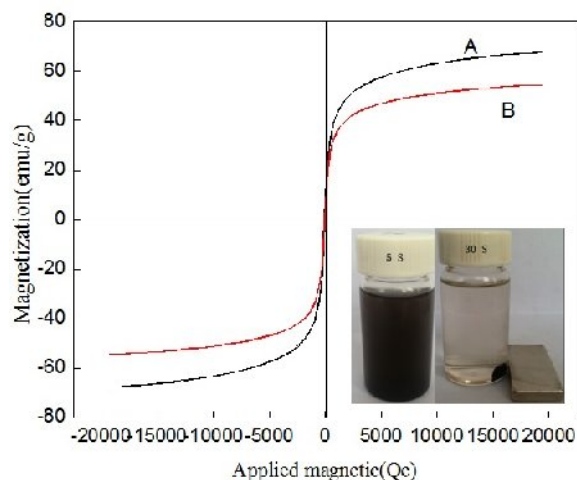The magnetic hysteresis loops of Fe_3O_4 and $Fe_3O_4@SiO_2$-MIPs were shown in Fig.6.

Fig.6:   Magnetic hysteresis loop of (A) Fe_3O_4 and (B) $Fe_3O_4@SiO_2$-MIPs microspheres.

In order to verify whether the composite adsorbent prepared is magnetic, 10 mg of $Fe_3O_4@SiO_2$-MIP samples were dispersed in distilled water by an ultrasonic bath for 10 min, then the mixture was found to be black suspension, as shown in the inset of Fig. 6, under the conditions of absence of an external magnet, a black and uniformly dispersed $Fe_3O_4@SiO_2$-MIPs suspension existed. When an external magnet was exerted, the black $Fe_3O_4@SiO_2$-MIPs were attracted to the wall of vial in a short time (about 30 s), indicating that the polymer microspheres prepared have good magnetism and can be rapidly separated by using adscititious magnetic field. This is because sulfonic group and carboxyl group of the iron dispersant PSMMA with a high charge density combined with the surface of the Fe_3O_4, Which increased the surface charge density of the microspheres and improved the dispersibility of the microspheres[10].

VSM is an important means to characterize the magnetic properties of the material. In this work, a vibrating sample magnetometer (VSM) was employed to measure the magnetic property of Fe_3O_4 and $Fe_3O_4@SiO_2$-MIPs. The magnetic hysteresis loops of the samples are illustrated in Fig. 6. The saturation magnetization values of Fe_3O_4 and $Fe_3O_4@SiO_2$-MIPs were 67.51 emu/g and 54.32 emu/g, respectively. The magnetization curves of the two samples were no magnetic hysteresis and symmetrical about the origin. Compared with the Fe_3O_4 particles, the saturation magnetization of $Fe_3O_4@SiO_2$-MIP reduced to 54.32 emu/g, and the residual magnetization decreased from 3.428 emu/g

to 2.11 emu/g, this is because the polymeric coating had effectively shielded the magnetic field, the coating increased the distance between Fe_3O_4 particles and reduced the magnetic coupling attractiveness between the particles. However, the $Fe_3O_4@SiO_2$-MIPs with less magnetite encapsulation also possesses enough magnetic response to meet the need of magnetic separation quickly [24]. Because the remanence magnetic (Mr) and coercivity (Hc) of $Fe_3O_4@SiO_2$-MIPs are all small, when the external magnetic field disappeared, $Fe_3O_4@SiO_2$-MIPs microspheres were able to uniformly dispersed into the medium again.

Thereby further illustrated that the formation of the SiO_2 layer and imprinted layer not only functionalized Fe_3O_4 particles, but also enhanced dispersibility of $Fe_3O_4@SiO_2$-MIPs, which facilitated magnetic separation and reusability [25]?

N$_2$ Adsorption–Desorption Isotherms

The nitrogen adsorption–desorption isotherms of $Fe_3O_4@SiO_2$-MIPs sample is depicted in Fig. 7.
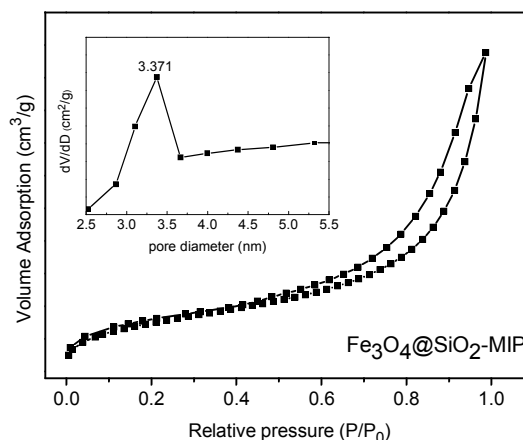

Fig. 7:   Nitrogen adsorption-desorption isotherms of $Fe_3O_4@SiO_2$-MIPs.

Fig. 7 showed that the adsorption isotherm was obviously not consistent with the desorption isotherm, the branch of the adsorption isotherm did not coincide with that of desorption, there was a hysteresis loop, this is because the nitrogen agglomerated in the pores of the surface of the sample to cause the phenomenon of capillary condensation. The $Fe_3O_4@SiO_2$-MIPs prepared is a kind of mesoporous adsorbent. For mesoporous adsorbents, the pore shape and pore size is different,

in the capillary hole, a concave liquid level formed due to the adsorption, and the vapor pressure being in balance with the liquid level is less than saturated vapor pressure of the planar liquid level at the same temperature. So the adsorbed nitrogen condensed to form liquid in the hole to result in the increase of adsorption capacity. The adsorption–desorption isotherms resemble type □ isotherm, in accordance with the International Union of Pure and Applied Chemistry (IUPAC) classification [26].

The inset in Fig. 7 showed the BJH pore size distribution plots of NP imprinted polymer adsorbent, we can see from it, average pore size of the sample was 3.71 nm, which attributed to mesopore capillary condensation adsorption. The BET specific surface area was 61.80 m^2/g, the Langmuir specific surface area was 101.24 m^2/g. Since the reticular crosslinking imprinted polymer with high specific surface area was formed on the surface of the sample, so the specific surface area of the sample was greatly increased [27].

Evaluation of Selectivity

In order to verify that the $Fe_3O_4@SiO_2$-MIP was selective for NP, 0.5 mmol/L of solutions of NP, phenol, bisphenol A (BPA) and octyl phenol (OP) were individually prepared for testing the binding characteristics of the $Fe_3O_4@SiO_2$-MIPs and $Fe_3O_4@SiO_2$-NIPs. Fig. 8 shows the adsorption efficiencies of NP, Phenol, BPA and OP on to the $Fe_3O_4@SiO_2$-MIP and $Fe_3O_4@SiO_2$-NIP.
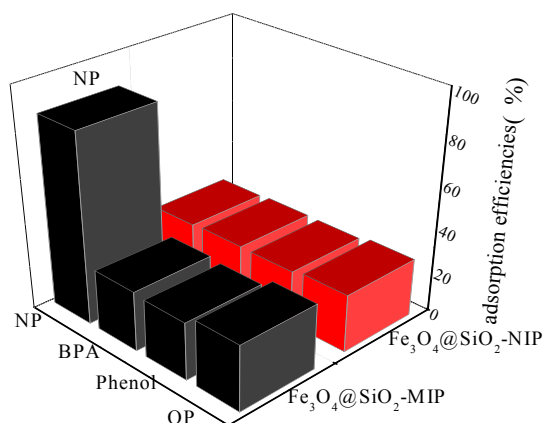

Fig. 8: Adsorption selectivity for NP and its analogs.

As shown in Fig.8, the adsorption efficiencies of BPA, phenol and OP on to the $Fe_3O_4@SiO_2$-MIPs are all remarkably smaller than that of NP, compared with the $Fe_3O_4@SiO_2$-NIPs, the higher selective recognition ability of the $Fe_3O_4@SiO_2$-MIPs for template molecule nonyl phenol was found.

In the process of synthesis of imprinting polymer, hydroxyl in template molecule NP bound with Nitrogen in monomer or oxygen in EGDMA via hydrogen bond, so that NP is fixed in the polymer network structure. After the template molecules being eluted, the functional group and the holes matched to the molecular size, chemical structure of template molecule NP was left in the polymer. The holes and functional group provided the recognition sites which can selectively bind with NP, so the specific adsorption of NP onto the $Fe_3O_4@SiO_2$-MIPs can be carried out [28]. NP and its analogues phenol, bisphenol A and octylphenol all have hydroxyl groups which can bind with functional group on monomer or EGDMA via hydrogen bond. But, their molecular size and chemical structure was unique and different from each other. This is why the adsorptive selectivity of molecularly imprinted polymer for NP is much higher than that for phenol, bisphenol A and octylphenol. Therefore, chemical structure, molecular size recognition and specific interaction of $Fe_3O_4@SiO_2$-MIPs toward the template molecules NP determine the adsorption selectivity. The results showed that the selective adsorption rate of NP reached 86.5%, and the adsorption rate of the analogous compounds was about 20~30%. It illustrated that $Fe_3O_4@SiO_2$-MIPs was more selective to the template NP.

The adsorption efficiency of NP on to the $Fe_3O_4@SiO_2$-NIPs was only 26.5%, which is close to the adsorption efficiencies of the analogous compounds selected on to the $Fe_3O_4@SiO_2$-NIPs; this can be attributed to the fact that the $Fe_3O_4@SiO_2$-NIPs had not generated specific recognition sites due to the absence of template during the preparation process.

Hydrogen bonds play an important role in the adsorption process, the carboxyl group on the polymer adsorbent bound with hydroxyl group of target molecule nonylphenol by the hydrogen bond [27], but the selective adsorption process is more complicated, there maybe exist other acting force except for hydrogen bond in the process of the adsorption, the adsorption mechanism should be

studied further.

In order to investigate the adsorption effect of NP with low concentration on to the molecular imprinted polymer, 20 mg $Fe_3O_4@SiO_2$-MIP was weighed into 20 mL of NP solutions with concentration of 0.5, 1.0, 1.5 and 2.0 mg/L, respectively. After shaking for 2 h at room temperature, the adsorption efficiencies were determined to be 96.2%, 95.4%, 91.8% and 90.3%, respectively. Thus, the $Fe_3O_4@SiO_2$-MIP is a promising adsorbent for removing NP with low concentration from aqueous solutions.

Conclusions

Magnetic molecularly imprinted polymer $Fe_3O_4@SiO_2$-MIPs can successfully be synthesized by using $Fe_3O_4@SiO_2$ modified by A-171 as the carrier, nonylphenol as template, 4-vpy as functional monomer, EGDMA as crosslinking agent and AIBN as initiator. The properties of the synthesized magnetic molecularly imprinted polymer reveal that it had higher selective recognition ability towards the template molecule nonylphenol comparable to that of the $Fe_3O_4@SiO_2$-NIPs. The particle diameter of the synthesized polymer $Fe_3O_4@SiO_2$-MIPs is 55-75 nm, the BET specific surface area was 61.80 m^2/g, the Langmuir specific surface area was 101.24 m^2/g, average pore size of the sample was 3.71 nm, and the saturation magnetization value was 54.32 emu/g. Under the conditions of this research, the adsorption efficiency of NP with concentration of 0.5 mmol/L on to the $Fe_3O_4@SiO_2$-MIPs can reach 86.5%, and for NP with low concentration (less than 2.0 mg/L), the selective adsorption rate reached more than 90%. The polymer $Fe_3O_4@SiO_2$-MIP synthesized has good magnetism and can be rapidly separated after being employed by using adscititious magnetic field. It has potential application value.

Acknowledgments

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