Preparation of magnetic porous aromatic framework for rapid and efficient removal organic pollutants from water

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Abstract

In this study, effort was made to prepare porous aromatic framework (PAF) with built-in magnetic nanoparticles (Fe$_3$O$_4$-PAF) as efficient adsorbent for the removal of organic pollutants from water. The Fe$_3$O$_4$-PAF showed good handleability and could be recovered easily by magnetic separation. As a proof of concept, the adsorption properties of Fe$_3$O$_4$-PAF was investigated to remove 2,4-dichlorophenol (2,4-DCP) and bisphenol A (BPA) from water. The Fe$_3$O$_4$-PAF showed fast adsorption rate, high adsorption efficiency and high adsorption capacities. It adsorbed 2,4-DCP (0.1 mmol L$^{-1}$) and BPA (0.1 mmol L$^{-1}$) with pseudo-second-order rate constant ($k_2$) of 2.1 and 3.54 g mg$^{-1}$ min$^{-1}$, respectively. According to Langmuir isotherm model, the maximum adsorption capacities of 2,4-DCP and BPA onto Fe$_3$O$_4$-PAF were calculated to be 234.74 and 233.65 mg g$^{-1}$, respectively. The Fe$_3$O$_4$-PAF also featured good tolerance to harsh conditions, facilitating its application in real water environment. It could be regenerated easily and reused multiple times without obvious losing its efficiency. In summary, this study provides a general and effective way to improve the handleability of PAFs and expands the practical application of PAF-based materials.

Keywords: Porous aromatic frameworks; Magnetic nanoparticles; Adsorption; 2,4-Dichlorophenol; Bisphenol A
Introduction

Water pollution is a serious environmental problem worldwide. Especially, the discharge of persistent organic pollutants into aquatic ecosystems, such as plasticizers, pesticides and pharmaceuticals, has posed a serious threat to human health.\textsuperscript{1} So, it is urgent to find ways for efficient removal of organic pollutants from water. And many kinds of methods, including physical, chemical and biological ones, have been developed for water remediation.\textsuperscript{2} Among them, adsorption is considered as one of the most effective ways, due to its easy operation, low cost, and versatile property.\textsuperscript{3}

Traditional adsorbents, such as activated carbons,\textsuperscript{4} zeolite,\textsuperscript{5} and clay,\textsuperscript{6} have been utilized for this aim. However, their application are hindered by the drawbacks of slow adsorption rate, low selectivity, limited adsorption capacities and energy-intensive regeneration. Recently, novel porous materials, such as covalent organic frameworks (COFs),\textsuperscript{7} porous organic polymers (POPs),\textsuperscript{8} metal-organic frameworks (MOFs),\textsuperscript{9} and porous aromatic frameworks (PAFs),\textsuperscript{10} have proved their competence in removing pollutants from water because of their appealing porous structural features. Among these porous materials, PAFs stand out due to their unusual robust structure and super stability. PAFs have attracted increasing interest, although the application of PAFs as excellent adsorbents is still in its initial stage.\textsuperscript{11} Based on PAF-1, Ma’s group prepared a series of PAFs functionalized with -SH, -CH$_2$N’(CH$_3$)$_3$OH, and amidoxime groups for the removal of Hg(II) ions,\textsuperscript{12} AuCl$_4^-$,\textsuperscript{13} and uranium\textsuperscript{14} from aqueous solutions, respectively. Long’s group introduced -SCH$_3$ groups into PAF-1,\textsuperscript{15} N-methyl-d-glucamine groups into PAF-1 and P2,\textsuperscript{16} for the
efficient capture of copper ion and removal of boric acid. This group also synthesized PAFs functionalized with carboxyl groups for efficient ammonia capture. Zhu’s group has applied nature PAFs or PAF-1@cellulose nanofibril composite aerogel as novel adsorbents for the efficient removal of organic contaminants, such as phenol, organic dyes, and bisphenol A. However, most of the PAFs in their powder forms are difficult to recycle, restricting their practical application.

To address this issue, Zhu’s group prepared PAF-45 modified electrospun fiber membrane for the efficient removal of pharmaceuticals and personal care products (PPCPs). The as-synthesized PAF-based composite showed improved handleability and great potential for large-scale applications. The introduction of magnetism is another way to overcome the restriction in powder materials recycle. For instance, Wang’s group reported the preparation of Fe₃O₄/MIL-101(Cr) as effective and reusable adsorbent to remove acid red 1 and orange G from water. Wang’s group described a magnetic covalent aromatic polymer as an efficient adsorbent for phenylurea herbicides. Zhang’s reported the preparation of 2D porous aromatic framework coated magnetic nanoparticles (PAF-6 MNPs) as an efficient solid-phase extraction sorbent for enrichment of trace organic pollutants. The core-shell magnetic nanoparticles showed excellent adsorption of phenols, polycyclic aromatic hydrocarbons and nitroaromatics based on π-π stacking and hydrogen-bond interactions. However, the application of magnetic PAFs are still few until now.

In this study, effort was made to prepare PAFs with build-in magnetic nanoparticles to enhance the handleability of PAFs for organic pollutants removal form water. Here,
Tetrakis(4-bromophenyl)methane (TBPM) was chosen as a tetrahedral monomer along with p-phenylenediboronic acid (PDA) as a linear linker to build the 3-D framework. As shown in Fig. 1, amino functionalized magnetic nanoparticles (Fe₃O₄@NH₂) was modified with phenylboronic acid groups to obtain Fe₃O₄@NH₂-CPBA. Then the Fe₃O₄@NH₂-CPBA reacted with TBPM and PDA through a one-pot reaction to obtain the magnetic PAFs (Fe₃O₄-PAF). As a proof of concept, 2,4-dichlorophenol (2,4-DCP) and bisphenol A (BPA) were chosen as model pollutants due to their notorious toxicity. The adsorption performance of the Fe₃O₄-PAF towards the target pollutants were investigated in detail.

**Experimental**

**Materials**

Tetrakis(4-bromophenyl)methane (TBPM) was purchased from Zhengzhou Alfa Chemical (Zhengzhou, China). Tetrakis(triphenylphosphine)palladium (0) [Pd(PPh₃)₄], activated carbon, humic acid (HA), bisphenol A (BPA), p-phenylenediboronic acid (PDA), 4-Carboxyphenylboric acid (CPBA) and 2,4-dichlorophenol (2,4-DCP) were bought from Aladdin Chemistry (Shanghai, China). Methanol of HPLC grade was bought from Dikma (Beijing, China). Water used in all of the chromatographic experiments was purified by a Milli-Q Ultrapure Water Purification System (Milford, USA). Aqueous solutions of 2,4-DCP and BPA were prepared using deionized water.

**Apparatus**

FT-IR spectra was obtained on a Tensor-37 FT-IR spectrometer (Bruker Optics, Ettlingen, Germany) in the wavenumber range of 600-4000 cm⁻¹. ¹H NMR spectra
was recorded on a Bruker Avance III HD 500 MHz instrument. Solid-state NMR spectra was recorded on a JEOL JNM-ECZ600R instrument. Transmission electron microscopic (TEM) investigations were carried on a FEI Tecnai G2 20 instrument. The N\textsubscript{2} adsorption-desorption analysis were performed on ASAP-2460 instrument at 77 K. Thermogravimetric analysis (TGA) was carried out on a TA Q500 thermogravimeter with a heating rate of 10 °C min\textsuperscript{-1} from room temperature to 800 °C under air. The samples were analyzed on an Agilent 1200 HPLC system. Analysis were performed at a flow rate of 1.0 mL min\textsuperscript{-1}. An Agilent XDB C18 column (250 mm × 4.6 mm, 5 μm) was used for all the chromatographic analysis, using methanol and water (80:20, v/v) as mobile phase. The detection wavelengths were 286 nm and 278 nm for 2,4-DCP and BPA, respectively. X-ray diffraction (XRD) spectre were recorded on a X’Pert\textsuperscript{3} Powder instrument.

\textit{Synthesis of the Fe\textsubscript{3}O\textsubscript{4}-PAF}

Aryl-Boroxine was synthesized from 4-carboxyphenylboric acid (Supporting Information section 1) and its structure was confirmed by 1H NMR.\textsuperscript{24} The Fe\textsubscript{3}O\textsubscript{4}@NH\textsubscript{2} was synthesized by solvothermal method (Supporting Information, section 2).\textsuperscript{25} Fe\textsubscript{3}O\textsubscript{4}@NH\textsubscript{2} (0.70 g) was dispersed into CH\textsubscript{2}Cl\textsubscript{2} (100 mL) by ultrasonication for 15 min, followed by the addition of triethylamine (4.0 mL) and the mixture was mechanically stirred for 2 h at ice-salt baths (-5 °C). Then, a solution of Aryl-Boroxine (2.10 g, 4.21 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (40 mL) was added, dropwise. The resulting solution was kept at -5 °C with ice-salt bath and stirred for 4 h. The product was washed with CH\textsubscript{2}Cl\textsubscript{2}, water and ethanol for 3 times each and dried at 80 °C under
vacuum overnight to obtain Fe$_3$O$_4$@NH$_2$-CPBA.

The Fe$_3$O$_4$-PAF was synthesized through Suzuki coupling reaction. Briefly, TBPM (0.65 g, 1.02 mmol) and PDA (0.34 g, 2.03 mmol) were dissolved into DMF (90 mL) in a 250 mL flask, followed the addition and dispersion of Fe$_3$O$_4$@NH$_2$-CPBA (0.4 g) under ultrasonic processing for 30 min. The flask was vacuumed and refilled with nitrogen three times. Subsequently, an aqueous solution of K$_2$CO$_3$ (2 mol L$^{-1}$, 8 mL) and Pd(PPh$_3$)$_4$ (96.0 mg, 83.2 µmol) were added to the mixture. The flask was vacuumed and refilled with nitrogen three times again and the mixture was mechanically stirred at 110 °C for 24 h. The precipitated product was separated by magnetic adsorption, washed with water, methanol, acetone, tetrahydrofuran (THF) and dichloromethane, respectively, and dried at 80 °C under vacuum overnight to obtain magnetic Fe$_3$O$_4$-PAF (0.87 g).

To fully verify the molecular structures of the magnetic PAF, a nature PAF without magnetism (P2) was synthesized using the same procedure except that the Fe$_3$O$_4$@NH$_2$ was not added (Supporting Information, section 3).$^{16}$

**Batch adsorption kinetic studies**

In a typical experiment, Fe$_3$O$_4$-PAF (10 mg) was added into a 10 mL aqueous solution of a certain pollutant at a given concentration with mechanical stirring. Samples were taken at appropriate time interval and the suspension was filtered. The concentration of the pollutant in the filtrate was determined with HPLC.

The concentration of pollutants were determined by HPLC and the pollutant removal efficiencies were calculated with the following equation:
Pollutant removal efficiency (%) = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)

where \( C_0 \) (mg L\(^{-1}\)) and \( C_t \) (mg L\(^{-1}\)) are the concentrations of pollutant before and after adsorption respectively. The amount of adsorbed pollutant was determined by the following equation:

\[ q_t = \frac{(C_0 - C_t)V}{m} \quad (2) \]

where \( q_t \) (mg g\(^{-1}\)) is the amount of pollutant adsorbed per gram of adsorbent at time \( t \) (min); \( V \) (L) is the volume of the solution; \( m \) (g) is the mass of the adsorbent.

**Adsorption isotherm studies**

Fe\(_3\)O\(_4\)-PAF (5 mg) was added into a 15 mL aqueous solution of 2,4-DCP or BPA at a given concentration (from 25 to 200 mg L\(^{-1}\)). The suspensions were shaken for 30 min and the adsorbent was collected by magnetic separation. The concentration of 2,4-DCP or BPA in the supernatant was determined with HPLC.

**Investigation of practical applicability**

For evaluation of the effect of pH on the adsorption performance, Fe\(_3\)O\(_4\)-PAF (10 mg) was added into a 10 mL (50 mg L\(^{-1}\), pH from 2 to 11) 2,4-DCP or BPA aqueous solution. The suspension was shaken for 30 min. The adsorbent was collected by magnetic separation and the concentration of 2,4-DCP or BPA in the supernatant was determined with HPLC.

To investigate the effect of ionic strength on the adsorption performance, Fe\(_3\)O\(_4\)-PAF (10 mg) was added to 10 mL (50 mg L\(^{-1}\), pH 7.0) 2,4-DCP or BPA aqueous solution with different NaCl concentrations (5-30 g L\(^{-1}\)). The suspension was
shaken for 30 min. The adsorbent was collected by magnetic separation and the concentration of 2,4-DCP or BPA in the supernatant was determined with HPLC. Similar experiments were conducted to investigate the effect of humic substance with the addition of HA (30-150 mg L\(^{-1}\)) to the 2,4-DCP or BPA solutions.

**Regeneration and reusability**

Fe\(_3\)O\(_4\)-PAF (10 mg) was added into 10 mL aqueous solution of BPA with different concentration. The mixture was mechanically stirred for 30 min and the adsorbent was settled down by a external magnet. The residual BPA concentration in the supernatant was determined by HPLC. The Fe\(_3\)O\(_4\)-PAF was regenerated by washing with 10 mL of methanol for 1h under mechanical stirring, followed by washed with water (5 mL) three times. The adsorption/desorption cycle was performed ten times.

**Results and discussion**

**Characterization of Fe\(_3\)O\(_4\)-PAF**

The morphology of Fe\(_3\)O\(_4\)-PAF was characterized by TEM analysis. As shown in Fig. 2a-d, the TEM images revealed that Fe\(_3\)O\(_4\)@NH\(_2\)-CPBA was well shaped as spheres with an average diameter about 60 nm. In contrary, the images shown in Fig 2e-h demonstrated that Fe\(_3\)O\(_4\)-PAF was composed of numerous nanoparticles dispersed throughout the PAF while the PAF shell with a thickness of about 25 nm surrounded the build-in magnetite nanoparticles. Compared with the TEM images of Fe\(_3\)O\(_4\)@NH\(_2\)-CPBA, the Fe\(_3\)O\(_4\)-PAF particles looked like much aggregation. This was due to the reactivity of Fe\(_3\)O\(_4\)@NH\(_2\)-CPBA and different particle could be fused together through Suzuki coupling reaction.
TGA was also carried out and the result demonstrated the high proportion of PAF in the Fe₃O₄-PAF and the excellent thermal stability of Fe₃O₄-PAF (Fig. S4). FT-IR (Fig S5a and Fig. S5b) and solid state $^{13}$C NMR (Fig. S5c) studies confirmed the successful preparation and chemical structure of the Fe₃O₄-PAF. N₂ adsorption-desorption studies (Fig S5d) revealed high surface area of Fe₃O₄-PAF and the coexistence of micropores and mesopores in Fe₃O₄-PAF, which endowed the Fe₃O₄-PAF with large surface areas and high accessibility, facilitating to obtain high adsorption capacity and improve the adsorption rate. XRD characterization was performed to investigate the crystallinity of Fe₃O₄-PAF and the results indicated its amorphous texture (Fig. S6).

**Adsorption kinetics**

Adsorption rate is a crucial factor of an adsorbent which determines industrial batch processing times. Adsorption kinetics of 2,4-DCP and BPA on Fe₃O₄-PAF were investigated with initial pollutants concentrations of 0.1 mmol L⁻¹ and 0.2 mmol L⁻¹. In addition, the adsorption kinetics on commercial activated carbon were also carried out for comparison. As shown in Fig. 3a, b, d and e, Fig. S7 and Fig. S8, the Fe₃O₄-PAF achieved adsorption equilibrium for 2,4-DCP and BPA in a significant shorter time than activated carbon. For example, the adsorption equilibrium time for 0.1 mmol L⁻¹ 2,4-DCP was only 1.98 min with adsorption efficiency reaching 99.59% and even for 0.2 mmol L⁻¹ 2,4-DCP, only 3.01 min was needed to reach adsorption equilibrium with adsorption efficiency as high as 96.73%. The adsorption kinetic was further quantified using pseudo-first-order and pseudo-second-order models, as shown
by the following equations: 

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$  \hspace{1cm} (3)

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$$  \hspace{1cm} (4)

where $q_t$ and $q_e$ (mg g$^{-1}$) are the adsorption capacity at certain time and equilibrium time, respectively, and $k_1$ (min$^{-1}$) and $k_2$ (g mg$^{-1}$ min$^{-1}$) are the pseudo-first-order model rate constant and the pseudo-second-order model rate constant, respectively.

The pseudo-first-order and pseudo-second-order fitting linear curves of 2,4-DCP and BPA on Fe$_3$O$_4$-PAF are shown in Fig. S9 and Fig. 3c and f while these fitting linear curves of 2,4-DCP and BPA on activated carbon are shown in Fig. S10, respectively. The corresponding kinetic parameters are calculated from the fitting linear curves and summarized in Table1 and Table S1. It is obvious that the correlation coefficients ($R^2$) of pseudo-second-order model was much greater than that of pseudo-first-order kinetic model, indicating that the pseudo-second-order model could better describe the adsorption kinetics of 2,4-DCP and BPA onto Fe$_3$O$_4$-PAF than pseudo-first-order model. From the comparison between Table1 and Table S1, it could be concluded that Fe$_3$O$_4$-PAF exhibits higher adsorption efficiency, faster adsorption kinetics and bigger pollutant uptakes at equilibrium than activated carbon.

**Adsorption isotherms**

Adsorption isotherms of 2,4-DCP and BPA on Fe$_3$O$_4$-PAF were investigated to obtain the maximum adsorption capacity and understand the interaction between the tested pollutants and Fe$_3$O$_4$-PAF. The adsorption isotherms for 2,4-DCP and BPA onto Fe$_3$O$_4$-PAF were shown in Fig. 4 and the equilibrium isotherm data are described by
Langmuir isotherm and Freundlich isotherm, as shown by the following equations:

\[ \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_l q_m} \]  
\( (5) \)

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  
\( (6) \)

Where \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration of the given pollutant, \( q_e \) (mg g\(^{-1}\)) is the amount of the pollutant adsorbed at equilibrium, \( q_m \) and \( K_l \) (L mol\(^{-1}\)) are the maximum adsorption capacity and binding energy related to Langmuir model, respectively. And \( K_f \) (mg\(^{-1}\)) and \( n \) are Freundlich equilibrium constant and heterogeneity factor, respectively. The linear fitting curves of the two isotherm models were shown in Fig. S11 while the isotherm parameters were summarized in Table 2.

According to the fitted curves in Fig. 6 and \( R^2 \) in Table 2, the adsorption isotherm data of 2,4-DCP and BPA were better depicted by Langmuir isotherm model, indicating a possible homogeneous and monolayer adsorption mechanism. The maximum adsorption capacities (\( q_m \)) for 2,4-DCP and BPA from Langmuir isotherm model are 236.23±1.71 and 234.08±4.95 mg g\(^{-1}\) and the obtained \( q_m \) were compared with other adsorbents. As illustrated in Table S2, the adsorption capacities towards 2,4-DCP and BPA were better than or comparable to most of the reported adsorbents.

**Investigation of practical applicability**

In real water environments, pH, ionic strength and humic substances can greatly affect the adsorption capacity of adsorbent. Fig. 5a displayed the effect of solution pH. It could be seen that the \( q_e \) of 2,4-DCP was not obviously influenced from pH 2 to 7 and the \( q_e \) of BPA almost kept constant from pH 2 to 9. The \( q_e \) of 2,4-DCP decreased
substantially when the pH exceeds 7 and the $q_e$ of BPA also showed decrease to some extent when the pH exceeds 9. This pH-dependent adsorption process is due to that 2,4-DCP (pKa = 7.9) and BPA (pKa$_1$ = 9.6 and pKa$_2$ = 10.2) are weak acids. So, 2,4-DCP was unionized in the pH range of 2 to 7 while BPA was unionized in the pH range of 2 to 9. However, when pH was greater than 7 for 2,4-DCP and greater than 9 for BPA, both of the adsorbates were ionized. In consequence, the partition of 2,4-DCP and BPA in water all increased, reducing the hydrophobic interaction between adsorbate and adsorbent.

The effect of ionic strength was investigated by adding NaCl into the adsorbates aqueous solutions. As shown in Fig. 7b, the $q_e$ of 2,4-DCP and BPA were not affected noticeably with increasing NaCl concentration, indicating that there was no competition between ions and the adsorbates and the electrostatic interaction was not involved in the adsorption of 2,4-DCP and BPA onto Fe$_3$O$_4$-PAF.

As for the investigation of the effect of humic substances, humic acid (HA) was selected as a representative humic substance. It is known that there are aromatic rings, carboxyl groups and phenolic hydroxyl groups in HA molecular and HA can occupy the active adsorption sites of adsorbent through hydrophobic interaction and π–π interaction. As shown in Fig. 7c, the $q_e$ of 2,4-DCP and BPA showed no obvious fluctuation with the increase of HA concentrations. This result indicated that the Fe$_3$O$_4$-PAF could provide adequate active adsorption sites for the efficient adsorption of 2,4-DCP and BPA under the experimental conditions, facilitating the practical application of Fe$_3$O$_4$-PAF in real water environments.
Regeneration and reusability

The regeneration and reusability of Fe₃O₄-PAF were evaluated using BPA as model pollutant. It was found that the adsorbed BPA on Fe₃O₄-PAF could be desorbed by washing with 10 mL of methanol for 1h under mechanical stirring. Followed by washing with water three times, the regenerated Fe₃O₄-PAF could be reused for the next adsorption cycle. It should be noticed that high consumption centrifugation, which was usually inevitable for powdery adsorbents, was avoided and the Fe₃O₄-PAF could be recovered easily by magnetic separation, as shown in Fig. 7d. As shown in Fig. 8, the $q_e$ for BPA at 0.1 mmol L⁻¹ and 0.2 mmol L⁻¹ showed almost no decrease after ten adsorption/desorption cycles. Even when the concentration of BPA was 0.4 mmol L⁻¹, the $q_e$ was only decrease about 1% after ten adsorption/desorption cycles. The FT-IR spectra shown in Fig. S12 further proved the efficient adsorption and readily desorption of BPA. The FT-IR spectra also revealed that the molecular structure of Fe₃O₄-PAF was maintained after ten adsorption/desorption cycles. The results indicated that Fe₃O₄-PAF had excellent stability and reusability.

Adsorption mechanism

The possible mechanism for the efficient adsorption of 2,4-DCP and BPA by Fe₃O₄-PAF was mainly hydrophobic interactions and π–π interactions. Besides, the molecular size of 2,4-DCP and BPA were 0.42 nm × 0.88 nm and 0.86 nm × 1.24 nm, respectively. The Fe₃O₄-PAF was microporous with the dominant micropore size at 0.6 nm and 1.2 nm. It could be expected that at least one dimension of 2,4-DCP and BPA were less than the micropore size of Fe₃O₄-PAF and 2,4-DCP and BPA could fill
in the micropores of Fe$_3$O$_4$-PAF. So, it was possible that pore-filling mechanism was also associated with the efficient adsorption of 2,4-DCP and BPA onto Fe$_3$O$_4$-PAF.

**Conclusions**

In conclusion, Fe$_3$O$_4$-PAF with build-in magnetic nanoparticles was successfully synthesized. The Fe$_3$O$_4$-PAF overcame the limitation of recycling associated with PAFs in power forms. It showed excellent adsorption properties towards 2,4-DCP and BPA, including fast adsorption rate, high adsorption efficiency and high adsorption capacity. It also demonstrated good practical applicability under harsh conditions. Besides, the Fe$_3$O$_4$-PAF could be regenerated easily and reused ten times without obvious losing its efficiency. In summary, the Fe$_3$O$_4$-PAF exhibited good handleability and great potential for the application in water remediation, providing a general way to improve the handleability of other PAFs and expanding the practical application of PAF-based materials.

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Table 1 Adsorption rate constants of 2,4-DCP and BPA on Fe₃O₄-PAF at different concentrations.

| mmol L⁻¹ | Pseudo-first-order model | | Pseudo-second-order model | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | qₑ(exp) | qₑ(cal) | k₁ | R² | qₑ(cal) | k₂ | R² | |
| | (mg g⁻¹) | (mg g⁻¹) | (min⁻¹) | | (mg g⁻¹) | (g mg⁻¹ min⁻¹) | |
| 2,4-DCP | | | | | | | | |
| 0.1 | 16.31 | 9.52±1.13 | 2.64±0.014 | 0.8806 | 16.34±0.0041 | 1.88±0.20 | 0.9999 | |
| 0.2 | 31.65 | 6.91±2.10 | 1.61±1.06 | 0.5141 | 31.21±0.81 | 0.50±0.082 | 0.9999 | |
| BPA | | | | | | | | |
| 0.1 | 22.83 | 6.15±0.99 | 1.91±0.42 | 0.4780 | 22.85±0.0060 | 3.33±0.83 | 1 | |
| 0.2 | 45.66 | 5.15±1.87 | 1.39±0.35 | 0.3921 | 45.69±0.032 | 3.59±0.94 | 1 | |
Table 2 Langmuir and Freundlich isotherm constants of (a) 2,4-DCP and (b) BPA onto Fe$_3$O$_4$-PAF.

| Pollutants | Langmuir isotherm | Freundlich isotherm |
|------------|-------------------|---------------------|
|            | $q_m$ (mg g$^{-1}$) | $K_L$ (L mol$^{-1}$) | $R^2$ | $K_f$ | $n$ | $R^2$ |
| 2,4-DCP    | 236.23±1.71        | (1.31±0.15)$\times10^4$ | 0.9930 | 50.21±4.48 | 3.14±0.17 | 0.9463 |
| BPA        | 234.08±4.95        | (3.86±0.12)$\times10^4$ | 0.9956 | 74.72±3.95 | 4.06±0.12 | 0.8831 |
Figure captions

Fig. 1 (a) Synthesis procedure of the phenylboronic acid modified magnetic nanoparticles (Fe₃O₄@NH₂-CPBA) and (b) Synthesis of Fe₃O₄-PAF by Suzuki coupling of Fe₃O₄@NH₂-CPBA, TBPM and PDA.

Fig. 2 TEM images of Fe₃O₄@NH₂-CPBA (a-d) and Fe₃O₄-PAF (e-h).

Fig. 3 Time-dependent adsorption of aqueous (a) 2,4-DCP (0.1 mmol L⁻¹), (b) 2,4-DCP (0.2 mmol L⁻¹), (d) BPA (0.1 mmol L⁻¹) and (e) BPA (0.2 mmol L⁻¹) by Fe₃O₄-PAF and activated carbon (each adsorbent, 1 mg mL⁻¹). Pseudo-second-order kinetic plots of (c) 2,4-DCP and (f) BPA onto Fe₃O₄-PAF.

Fig. 4 Adsorption isotherms of (a) 2,4-DCP and (b) BPA onto Fe₃O₄-PAF.

Fig. 5 The effect of solution pH (a), ionic strength (b) and humic substances (c) on the 2,4-DCP and BPA adsorption by Fe₃O₄-PAF. The recovery of Fe₃O₄-PAF by magnetic separation (d).

Fig. 6 Reusability of Fe₃O₄-PAF for the adsorption of BPA at different concentrations.
Figures:

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