A Novel Magnetic Graphene Oxide Composite Absorbent for Removing Trace Residues of Polybrominated Diphenyl Ethers in Water

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Abstract: The purpose of the study was to develop a facile method for the fabrication of a stable and reusable magnetic graphene composite absorbent to remove trace levels of polybrominated diphenyl ethers in water treatment. The poly cationic $\text{Fe}_3\text{O}_4@\text{PDDA}$ (poly(diallyldimethyl ammonium chloride) (PDDA)) core-shell structured nanoparticles were first synthesized, and then, DNA was laid on the surface of graphene oxide (GOx) to prepare the polyanionic GOx@DNA composite. The above materials were then mixed together and adhered together through sol-gel technology. Thus, the $\text{Fe}_3\text{O}_4@\text{PDDA}/\text{GOx}@\text{DNA}$ composite absorbent was prepared. Its performance was tested by disperse solid phase extraction and gas chromatography/mass spectrometric (GC/MS) for removing six kinds of indicative polybrominated diphenyl ethers (BDEs) in water samples. The removal percentages of several real samples for six kinds of BDEs (BDE17, BDE28, BDE 71, BDE 47, BDE 66, BDE 100) at the ng/mL order of magnitude were in the range of 88.2%–99.1%. The removal percentage still reached 80.0% when the adsorbent was reused at least 20 times. The results suggested that the magnetic absorbent can obviously remove trace levels of BDEs from large volumes of aqueous solutions in environmental pollution cleanup with high removal efficiency.
1. Introduction

Polybrominated biphenyls (BDEs) have been widely applied in many areas, including heat transfer fluids and dielectric fluids [1]. However, they are a typical class of the persistent organic pollutants (POPs) that cause great harm to the environment, as well as human health, due to their toxicity, high stability and biomagnification through the food chain [1]. Because of their low aqueous solubility and bioavailability, BDEs are resistant to biodegradation and are difficult to be removed by conventional physicochemical techniques, such as coagulation, flocculation, sedimentation and filtration [2]. Therefore, it is necessary to remove organic dyes in environmental water. Adsorption has been regarded as one of the most effective physical processes for removing BDEs in wastewaters, since it can produce high quality water and also be a process that is economically feasible. Activated carbon (AC) is the most widely used commercially available absorbent [3]. However, difficult regeneration and lower absorption capacity limits its application in waste water treatment [4].

Carbon nanotubes and graphene oxide (GOx) are a class of electron-rich carbon adsorbents with a large delocalized π-electron system, which shows promising applications in water treatment [5]. Due to graphene oxide’s unique plate structure and properties, including large specific surface area, excellent stability and rich functionalities [6], organic compounds with a benzene ring can be strongly adsorbed on GOx. However, a major defect comes from the difficulties that are associated with the separation of water-insoluble GOx from water solutions after absorption procedures. Magnetic composite materials also have many advantages, such as simple separation, high adsorption capacity and cyclic utilization, which can greatly expand their application in environmental purification. Magnetic separation has been developed to facilitate the collection of GOx [7,8].

Various magnetic materials can be used as adsorbents. Fe₃O₄@PDDA (poly(diallyldimethyl ammonium chloride) (PDDA)) with a core-shell structure can form magnetic nanoparticles that reveal excellent dispersion and chemical stability, which are not easy to reunite and for saturation magnetization. The sol-gel technique will be selected as the preparation method for combining Fe₃O₄@PDDA with positive charges and GOx@DNA, which has a large amount of negative charges [7,8]. In the preparation process, oppositely-charged species are deposited on a carrier in sequences through electrostatic assembly [8]. In this study, the Fe₃O₄@PDDA core-shell-structured nanoparticles were modified with GOx@DNA through sol-gel technology in order to improve their stability and adsorption capacity. Herein, the magnetic microspheres with Fe₃O₄ as the core and PDDA on its surface as a shell were synthesized through the sol-gel approach, which can obtain polycationic magnetic microspheres (Fe₃O₄@PDDA). The above materials were modified with polyanionic graphenes, which were modified by negative DNA. In the composites, the polyelectrolyte layer cannot only enhance the adhesive strength between GOx@DNA and Fe₃O₄@PDDA, but also increase the amount of the GOx on it.

**Keywords:** graphene oxide; magnetic disperse solid phase extraction; water treatment; sol-gel technology; polybrominated diphenyl ethers
Combined with magnetic nanocomposites (Fe$_3$O$_4$@PDDA/GOx@DNA) as adsorbents, the technique of magnetic solid-phase extraction (mSPE) was chosen for an effective pretreatment assay to enrich and purify analytes in samples with a complex matrix [9–15]. With the magnetic property, the new absorbent using mSPE could avoid time-consuming procedures and be performed directly to pretreat crude samples without the need for centrifugation or filtration, due to the facile magnetic separation [10]. The aim of this study was to develop a simple, rapid, inexpensive and robust methodology to remove BDEs in real water samples. The proposed methodology included magnetic nanocomposites (Fe$_3$O$_4$@PDDA/GOx@DNA) prepared by sol-gel technology for removing BDEs in environmental water samples. The adsorption experiment showed that the magnetic nanocomposites could be reused at least 20 times without a significant loss of the clean-up efficiency. The adsorbents were successfully employed for removing the trace level of BDEs in real water samples.

2. Materials and Methods

2.1. Chemicals

2,4-Dibromophenyl 2-bromophenyl ether (BDE17), 2,4,4′-tribromodiphenyl ether (BDE28), 2,3′,4′,6-tetramethylphenyl ether (BDE 71), 2,2′,4,4′-tetrabromodiphenyl ether (BDE 47), 2,3′,4,4′-tetramethylphenyl ether (BDE 66) and 2,2′,4,4′,6-pentabromodiphenyl ether (BDE 100) were obtained from Accu Standard Inc. (New Haven, CT, USA). Ct-DNA (Lot: D4522-1MG, Sigma, New York, NY, USA) and poly(diallyldimethyl ammonium chloride) (PDDA, 20%, w/w, in water, MW = 100,000–200,000) were purchased from Sigma-Aldrich (New York, NY, USA). The carboxyl of graphenes (purity > 95 wt%, ASH < 1.5 wt%, SSA > 500 m$^2$/g) were purchased from Nanoport. Co. Ltd. (Shenzhen, China). Ferric chloride (FeCl$_3$·6H$_2$O), ammonia (28%), n-hexane, ethylene glycol, tetraethyl orthosilicate (TEOS), sodium acetate and dichloromethane were purchased from Beijing Chemicals Corporation (Beijing, China). The syringe filters were purchased from Xingya (Shanghai, China). All other chemicals were used as received without further purification. The water in this work was deionized water.

2.2. Preparation of Fe$_3$O$_4$@PDDA/GOx@DNA Nanoparticles

2.2.1. Synthesis of Fe$_3$O$_4$ Nanospheres

The magnetic nanoparticles were prepared based on the previously reported hydrothermal procedures [11]. 5.75 g FeCl$_3$·6H$_2$O and 15.33 g of sodium acetate were dissolved in 320 mL of ethylene glycol under mechanical stirring. The obtained homogeneous yellow solution was transferred to a Teflon-lined stainless steel autoclave, sealed and heated at 200 °C for 8 h. The obtained black magnetite precipitate was washed with ethanol and deionized water three times, then dried at 60 °C under vacuum.

2.2.2. Synthesis of Fe$_3$O$_4$@PDDA Nanospheres

The Fe$_3$O$_4$@PDDA nanospheres were prepared according to the previously reported sol-gel method [12]. Briefly, 0.5 g of dry Fe$_3$O$_4$ particles were firstly pretreated with 0.1 M HCl aqueous
solution (100 mL) by ultrasonication for 15 min. Moreover, pH 7.0 PBS was added to maintain the neutral characteristics. The resulting suspension was stirred in 0.1 mol/L PDDA for 6 h at room temperature. The obtained Fe₃O₄@PDDA nanospheres were magnetically separated, washed with ethanol and deionized water, then dried at 60 °C in vacuum for 2 h. The black precipitate was washed with deionized water three times and dried at 60 °C in vacuum for 2 h.

2.2.3. Synthesis of Fe₃O₄@PDDA/GOx@DNA Nanoparticles

Graphene was firstly purified in 0.5 M HCl solution by ultrasonication for 4 h. The resulting material was washed with water several times and dried under vacuum at 60 °C overnight [13]. 50 mg purified GOx were dispersed in sodium chloride aqueous solution (0.5 mol/L, 100 mL). Then, 6 mL of DNA solution (20%) were added dropwise under vigorous stirring. The mixture was centrifuged at 5000 rpm for 5 min and washed with deionized water to remove the superfluous DNA. The obtained GOx/DNA with a positive charge was dried at 60 °C in vacuum overnight.

Fifty milligrams of Fe₃O₄@PDDA nanoparticles with a negative charge were dispersed in 100 mL of water. Then, 50 mg of dry GOx/DNA were added with mechanical stirring. After reaction for 60 min, the product was collected with a magnet, then washed with ethanol and deionized water, dried at 60 °C in vacuum for 2 h. The preparation process is shown in Figure 1.

![Figure 1. Synthesis strategy of Fe₃O₄@PDDA /GOx@DNA.](image)

2.3. The Removal Experiment for BDEs in Waters

Sample solutions (1000 ng/mL) with six kinds of BDEs were prepared in isoctane and stored at 4 °C. All of the working solutions of BDEs were 100 ng/mL and prepared daily by appropriate dilution of the stock solutions with n-hexane. All glassware used in the study was soaked and washed in acetone, then rinsed with n-hexane and dried at 100 °C for 4 h.

For the adsorption steps, 30 mg of the adsorbents (Fe₃O₄@PDDA/GOx@DNA) were rinsed and activated in 1 mL of methanol, then uniformly dispersed into the 100-mL filtered water sample in a beaker (100 mL of deionized water spiked with 10 ng/mL of BDEs were used, and all of the experiments were performed in triplicate). The mixture was stirred vigorously at 300 rpm for 30 min. Subsequently, a strong magnet was placed at the bottom of the beaker, so that the adsorbents were isolated from the solution. The solution became limpid after about 1 min. The procedures are shown in Figure 2.
For the desorption step, firstly, the supernatant was decanted carefully with the magnet, and the pre-concentrated analytes were transferred to the syringes of an organic membrane (0.45 μm) and dried at 60 °C under vacuum for 4 h. Secondly, the adsorbed compounds were eluted from the adsorbents with 10 mL of a mixture of n-hexane:dichloromethane (40/60, v/v) as the elute. The flow rate was controlled at 2 mL/min, and the eluates were collected with a centrifugal tub. Thirdly, the adsorbents were dried with nitrogen to remove the dichloromethane and n-hexane. Then, the residue was dissolved in 1 mL of n-hexane with 0.5 mL of concentrated sulfuric acid to further acidification. Finally, the mixed solution was centrifuged for 10 min, and the supernatant liquid was stored in a fridge overnight. One microliter of this solution was injected into the GC/MS system for analysis. The experiment process is shown in Figure 2. The overall procedure took place at room temperature. The BDE removal percentage was calculated using Equation (1) [16].

\[
\text{Removal percentage (\%)} = \frac{C_0 - C_i}{C_0} \times 100\%
\]

where \(C_0\) is the original concentration of BDEs and \(C_i\) represents the residual concentration of BDEs after extraction, respectively.

2.4. Real Sample Preparation

Water samples were collected in Ningbo in September, 2013. Tap water samples were taken from our laboratory in Yongjiang River, and water samples were acquired from Jiangbei District (Ningbo). All samples were collected randomly and filtered through 0.45-μm membranes to remove suspended particles.

3. Results and Discussion

3.1. Characterization of Adsorbents

SEM figures were used to characterize the morphology of \(\text{Fe}_3\text{O}_4\), \(\text{Fe}_3\text{O}_4@\text{PDDA}\), \(\text{GOx}@\text{DNA}\) and \(\text{Fe}_3\text{O}_4@\text{PDDA/GOx}@\text{DNA}\) (Figure 3a–d). Figure 3a shows that the mean particle size of \(\text{Fe}_3\text{O}_4\) NPs was about 300 nm. Figure 3b shows the \(\text{Fe}_3\text{O}_4@\text{PDDA}\) cross-linked together, which proved that PDDA as a polymer was successfully coated onto \(\text{Fe}_3\text{O}_4\) NPs. The tree-like structure of SEM images
(Figure 3c) of GOx@DNA showed that GOx@DNA was successfully synthesized. Both the feathery and spherical composite structures in Figure 3d also proved that GOx@DNA was successfully absorbed on the surface of Fe₃O₄@PDDA through sol-gel technology.

**Figure 3.** SEM images of: (a) Fe₃O₄; (b) Fe₃O₄@PDDA; (c) GOx@DNA; (d) Fe₃O₄@PDDA/GOx@DNA.

![SEM images](image)

Figure 4 displayed the IR spectra of GOx, Fe₃O₄, Fe₃O₄@PDDA and Fe₃O₄@PDDA/GOx@DNA. Strong absorption bands between 3300 and 3500 cm⁻¹ were due to O–H stretching vibration. The types of peaks shown by GOx were between 1300 and 1100 cm⁻¹, which were due to the stretching of phenyl-carbonyl C–C bonds. The 2924 and 2820 cm⁻¹ bands were due to C–H (Figure 4a). As shown in Figure 4b, the peaks at 584 and 467 cm⁻¹ were the stretching vibration due to the Fe–O bonds. Compared to the two spectra (Figure 4b,c), the Fe–O peaks shift to 580 and 473 cm⁻¹ (Figure 4c). From Figure 4c,d, we could see that the C–H stretching vibrating band of Fe₃O₄@PDDA/GOx@DNA at 2924 and 2820 cm⁻¹ appeared. All of these demonstrated that GOx was successfully modified to the Fe₃O₄@PDDA through sol-gel technology.

Figure 5 shows the magnetization curves of Fe₃O₄, Fe₃O₄@PDDA and Fe₃O₄@PDDA/GOx@DNA at room temperature. Maximum saturation magnetization of Fe₃O₄@PDDA was measured at 25.4 emu/g, which was lower than that of magnetic Fe₃O₄ alone (48.2 emu/g). This might be due to the nonmagnetic surface of the PDDA. The saturation magnetization of Fe₃O₄@PDDA/GOx@DNA was at 18.2 emu/g. Although the addition of the nonmagnetic part (GOx) led to a decrease in the saturation magnetizations, the obtained Fe₃O₄@PDDA/GOx@DNA still had a high saturation magnetization.
It was observed that Fe$_3$O$_4$@PDDA/GO$_x$@DNA adsorbents could be dispersed into water solution readily. Thus, the magnetic adsorbents loaded with analytes could be isolated from the matrix conveniently by using an external magnet when necessary.

**Figure 4.** IR spectra of: (a) GO$_x$; (b) Fe$_3$O$_4$; (c) Fe$_3$O$_4$@PDDA; (d) Fe$_3$O$_4$@PDDA/GO$_x$@DNA.

![IR spectra of GO$_x$, Fe$_3$O$_4$, Fe$_3$O$_4$@PDDA, Fe$_3$O$_4$@PDDA/GO$_x$@DNA.]

**Figure 5.** Vibrating sample magnetometer (VSM) magnetization curves of: (a) Fe$_3$O$_4$; (b) Fe$_3$O$_4$@PDDA; (c) Fe$_3$O$_4$@PDDA/GO$_x$@DNA.

![Vibrating sample magnetometer (VSM) magnetization curves of Fe$_3$O$_4$, Fe$_3$O$_4$@PDDA, Fe$_3$O$_4$@PDDA/GO$_x$@DNA.]

The XRD pattern in Figure 6a–d showed the crystal structure of the materials, GO$_x$, Fe$_3$O$_4$, Fe$_3$O$_4$@PDDA and Fe$_3$O$_4$@PDDA/GO$_x$@DNA, respectively. The well-resolved diffraction peak revealed the crystallinity of the GO$_x$, which was located at $2\theta = 22.5^\circ$. There were several relatively strong diffraction peaks at $2\theta = 30.2^\circ$, $35.5^\circ$, $43.3^\circ$, $57.3^\circ$ and $62.7^\circ$ in Figure 6b, which were quite
similar to those of the Fe₃O₄ nanoparticles reported by other groups [14]. From the XRD pattern of Fe₃O₄@PDDA/GOx@DNA in Figure 6e, the main characteristic peaks of Fe₃O₄ still remained and the strong diffraction peak at 2θ = 22.5° (GOx) appeared again, which indicated that the composite was composed of Fe₃O₄@PDDA and GOx@DNA.

Figure 6. X-ray diffraction (XRD) patterns of: (a) GOx; (b) Fe₃O₄; (c) Fe₃O₄@PDDA; (d) Fe₃O₄@PDDA/GOx@DNA.

3.2. Kinetic Study

As shown in Figure 7a, the kinetics of the uptake of BDE28 by the Fe₃O₄@PDDA/GOx@DNA (100 mL of deionized water spiked with 152 ng/mL onto 30 mg of the adsorbents) was studied from the adsorption rate of BDE28 to the adsorbents, which showed two stages, a quick stage at the beginning and a slow stage before the equilibrium. The results (Figure 7a) showed that the rate of adsorption for BDE28 was very rapid in the first 20 min; thereafter, it decreased gradually, until it reached a plateau after 30 min, indicating the equilibrium of the system. The phenomena of the adsorption kinetics may be due to the adsorption of BDE28 on the exterior surface of the adsorbent at the initial period of contact time. When the adsorption on the exterior surface reached the saturation point, BDE28 reached into the pores of the adsorbent. In order to elucidate the adsorption process, the results were fitted using the Lagergren first-order model [17] and the pseudo second-order model [18]. The Lagergren first-order model can be expressed as follows:

$$\ln (Q_{eq} - Q_t) = \ln Q_1 - k_1 t$$

where $k$ (min⁻¹) is the rate constant of adsorption and $Q_t$ (mg g⁻¹) and $Q_{eq}$ (mg g⁻¹) represent the amount of the dye adsorbed at any time $t$ (min) and at equilibrium, respectively. The rate constant $k$ can be determined from the slope of the plot obtained by plotting $\ln (Q_{eq} - Q_t)$ versus $t$.

The pseudo-second-order model equation is given as:
where \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) are the rate constant of the Lagergren first-order model and pseudo-second-order model, \( Q_t \) (mg g\(^{-1}\)) and \( Q_{eq} \) (mg g\(^{-1}\)) represent the amount of the dye adsorbed at any time \( t \) (min) and at equilibrium and \( Q_1 \) (mg g\(^{-1}\)) and \( Q_2 \) (mg g\(^{-1}\)) are the calculated adsorption capacity of the Lagergren first-order model and pseudo-second-order model.

The Lagergren first-order rate constant \( k_1 \) and \( Q_1 \) can be determined from the intercept and slope of the plot obtained by plotting \( \ln (Q_{eq} - Q_t) \) versus \( t \); the pseudo-second-order rate constant \( k_2 \) and \( Q_2 \) can be determined from the intercept and slope of the plot obtained by plotting \( t/Q_t \) versus \( t \).

The calculated parameters for Lagergren first-order model and pseudo-second-order model and the correlation coefficients \((r^2)\) are listed in Table 1.

| Sample | \( Q_{eq} \) (mg g\(^{-1}\)) | Lagergren First-Order Model | Pseud Second-Order Model |
|--------|---------------------|-----------------------------|-------------------------|
|        | \( Q_1 \) (mg g\(^{-1}\)) | \( K_1 \) (min\(^{-1}\)) | \( r^2 \) | \( Q_2 \) (mg g\(^{-1}\)) | \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) | \( r^2 \) |
| BDE28  | 49.1                | 49.0                        | 0.387                   | 0.998                      | 49.1                | 0.023                        | 0.984 |

Figure 7. The effect of adsorption time on the adsorption capacity.

A comparison of \( Q_{eq} \) data (Table 2) shows that the calculated \( Q_2 \) values of the pseudo-second-order equation are generally closer to the experimental \( Q_{eq} \) values compared to the calculated \( Q_1 \) values of the Lagergren first-order equation. The correlation coefficients for the first order kinetic model obtained for all of the studied BDE28 were above 0.998. Therefore, the adsorption process studied follows the Lagergren first-order model better. Based on the assumption of the pseudo-second-order model [18], it can be concluded from the experimental result that the adsorption of cationic BDE28 on G-SO\(_3\)H/Fe\(_3\)O\(_4\) is mainly due to chemical adsorption [19].
Table 2. Removal percentages of six kinds of BDEs from real water samples spiked with target analytes.

| Analytes            | BDE17   | BDE28   | BDE71   | BDE47   | BDE66   | BDE100  |
|---------------------|---------|---------|---------|---------|---------|---------|
| Found (ng/mL)       | ND      | ND      | ND      | ND      | ND      | ND      |
| Removal percentages |         |         |         |         |         |         |
| (%)                 |         |         |         |         |         |         |
| (Add 5 ng/mL)       |         |         |         |         |         |         |
| Tap water            | 92.5 ± 2.3 | 94.1 ± 3.1 | 87.8 ± 2.9 | 93.2 ± 2.8 | 93.3 ± 3.9 | 90.2 ± 3.4 |
| Zhenhai River Water 1 | 90.2 ± 3.4 | 93.2 ± 4.8 | 92.1 ± 4.3 | 93.4 ± 3.2 | 89.5 ± 3.5 | 90.4 ± 3.3 |
| Removal percentages | 89.6 ± 1.8 | 89.7 ± 3.4 | 90.6 ± 3.4 | 90.7 ± 2.1 | 98.8 ± 3.4 | 93.5 ± 3.2 |
| (%)                 | (Add 5 ng/mL) |         |         |         |         |         |
| Yongjiang River water | 92.8 ± 2.1 | 97.5 ± 1.2 | 93.3 ± 3.2 | 92.4 ± 4.3 | 94.1 ± 3.1 | 93.3 ± 1.7 |
| Removal percentages | 92.3 ± 2.8 | 99.5 ± 2.9 | 94.1 ± 5.8 | 92.5 ± 4.7 | 92.3 ± 4.9 | 89.1 ± 2.8 |
| (%)                 | (Add 5 ng/mL) |         |         |         |         |         |

ND: not detected.

3.3. Adsorption Isotherms

The adsorption isotherm gave the most significant information, which pointed out how the adsorbate molecules were distributed between the liquid phase and solid phase when the adsorption process reaches equilibrium. The adsorption isotherm helped to disclose the adsorption mechanism of BDE28 onto Fe₃O₄@PDDA/GOx@DNA. According to previous reports, the stronger adsorption of aromatic compounds on GOx was attributed to the π–π interaction. In addition, the hydrophobic effect was another important factor that was responsible for the adsorption on GOx. The adsorption of BDE28 on Fe₃O₄@PDDA/GOx@DNA was studied under ambient conditions using a batch technique. In the removal of BDE28 from aqueous solutions, the amount of adsorbents used in the cleaning procedure was vital for the economic application. In our study, the experimental data of BDE28 were fitted by employing the Langmuir and Freundlich model [20–22].

The form of the Langmuir isotherm can be represented by the following equation:

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{bq_{\text{max}}} \cdot \frac{1}{c_e}
\]  (4)

Here, \(q_{\text{max}}\) and \(b\) were Langmuir constants related to the adsorption capacity and adsorption energy, respectively. The standard correlation coefficient \((R^2)\) was employed to compare the goodness of fit between model prediction and experimental data. The calculated values of \(q_{\text{max}}\) and \(1/b\) were 49.1 mg/g and 4.2, respectively; \(R^2\) was 0.998. The Freundlich isotherm model is expressed as follows:

\[
\log q_e = \log k_F + n \log c_e
\]  (5)

where \(k_F\) represents the adsorption capacity when the adsorbate equilibrium concentration equals one and \(n\) represents the degree of adsorption dependence at the equilibrium concentration.
The experimental data was not in good agreement with the Freundlich isotherm model after calculation (Figure 8). The absorbent had a high nitrogen BET specific area of ~310 m²/g (calculated in the linear relative pressure range from 0.1 to 0.3) [22]. The average pore size was 3 nm, which showed it was microporous.

**Figure 8.** Freundlich isotherm for the adsorption of BDE28 to Fe₃O₄@PDDA/GOx@DNA.

![Graph showing Freundlich isotherm](image)

Y = -0.213 + 0.482X (R = 0.997)

3.4. Effect of Adsorption Conditions

In this experiment, several parameters, including adsorption conditions and desorption conditions, were discussed to achieve the best removal efficiency for BDEs. To study the extraction performance of the mSPE under different experimental conditions, 100 mL of deionized water spiked with 10 ng/mL of BDEs were used, and all of the experiments were performed in triplicate. The results were used as a means of optimization.

3.4.1. Adsorption Time

In order to assess the ability of the Fe₃O₄@PDDA/GOx@DNA to adsorb BDE28, equilibrium adsorption time profiles were derived by increasing the adsorption time of 100 mL of the water sample. The results showed that there was a rapid removal efficiency when the adsorption time increased from 5 to 50 min. After 30 min, the maximum removal percentages were obtained for BDE28, which were close to 90% (Figure 9). Consequently, an adsorption time of 30 min was selected for further study.
3.4.2. Amount of the Adsorbents

To achieve the highest maximum removal percentages towards the target analytes, the amount of Fe₃O₄@PDDA/GOx@DNA was increased from 5 mg to 50 mg. The overall recoveries were augmented significantly when the amount of adsorbents increased up to 20 mg; when the amount of adsorbents achieved 30 mg (Figure 10), the removal percentages of BDEs were exceeded by 85%.

Figure 10. The effect of the amount of the adsorbents on the recovery of BDE28 by Fe₃O₄@PDDA/GOx@DNA.
The overall removal percentages were made to remain unchanged by further increasing the amount of the adsorbents, indicating the remarkable enrichment ability of Fe$_3$O$_4$@PDDA/GOx@DNA as adsorbents. Thirty milligrams of the adsorbents were employed in the study by considering the sensitivity and consumption of the material.

3.4.3. Effect of the Solution pH

The pH was adjusted between 3.0 and 11.0 by the addition of 0.1 M HCl or NaOH. The adsorption percentage of BDEs on Fe$_3$O$_4$@PDDA/GOx@DNA fluctuated very little with the recovery ranging from 80% to 85% in a pH range of 5–10, with a lower recovery between pH 2 to 3 (Figure 11). All of this suggested that the analytes could efficiently be adsorbed onto the adsorbent at any pH of the real neutral aqueous solutions. Since the pH of the real water samples was generally in the range 5.0–8.0, there was no need to adjust the pH of the sample solution before adsorption. As seen from our experiment, the absorbent was suitable for PCB pollution cleanup in real work.

Figure 11. The effect of pH on the recovery of BDE28 by Fe$_3$O$_4$@PDDA/GOx@DNA.

3.5. The Reusability of the Absorbent

The recycling of the nanoparticle adsorbents was studied to verify the chemical stability of the magnetic graphene composites. The Fe$_3$O$_4$@PDDA/GOx@DNA was prepared by a self-assembly technique, and the Fe$_3$O$_4$@PDDA/GOx was prepared by in situ synthesis. The adsorbents used in the adsorption procedure were treated with 2 mL of dichloromethane by ultrasonication for 10 min and then washed by 2 mL of n-hexane before being applied to the next adsorption procedure. The Fe$_3$O$_4$@PDDA/GOx@DNA adsorbents could be reused 20 times without losing much of the removal percentages of analytes (>80%, Figure 12). However, we found that if the absorbent used Fe$_3$O$_4$@SiO$_2$ as the carrier, it can be reused for at least 50 times, because it has good dispersibility.
Figure 12. The recycling efficiency vs. cycle number after removing BDE28 by Fe$_3$O$_4$@PDDA/GO$_x$@DNA.

![Graph showing recycling efficiency vs. cycle number](image)

3.6. The Application of Adsorbent in Environmental Water Samples

To test the removal efficiency of Fe$_3$O$_4$@PDDA/GO$_x$@DNA, tap water, Zhenhai River 1 and its spiked water samples (spiked with 5 ng/mL of BDEs), as well as Yongjiang River water were used as the analysis object by this paper. As shown in Table 2 and Figure 13, the results indicated that Zhenhai River water was contaminated by BDE 17, BDE28 and BDE 71 (Figure 13). The data of spiked water samples showed that Fe$_3$O$_4$@PDDA/GO$_x$@DNA was a suitable material to remove BDEs in environmental water samples. The conventional method of C18 SPE (solid phase extraction with a C18 membrane) was used in our experiment, and the result implied that the adsorbents have excellent removal efficiency (Table 3).

Figure 13. Chromatographs of (a) Zhenhai River 1 sample and (b) the river sample spiked with 5 ng/mL of BDEs.

![Chromatographs of Zhenhai River samples](image)
Table 3. The detection results of BDEs in Zhenhai River 2 water by the conventional method of C18 SPE and the proposed adsorbent in our manuscript.

| Analytes in Zhenhai River 2 | BDE17 | BDE28 | BDE71 | BDE47 | BDE66 | BDE100 |
|----------------------------|-------|-------|-------|-------|-------|--------|
| C18-SPE Found (ng/mL)      | 0.50  | 0.58  | 0.69  | ND    | ND    | ND     |
| This work adsorbent Found (ng/mL) | 0.55 | 0.54  | 0.78  | ND    | ND    | ND     |

4. Conclusions

In the present work, novel magnetic nanocomposites (Fe₃O₄@PDDA@DNA/GOx), using the facile layer-by-layer self-assembly method, were used as the adsorbents for removing six kinds of BDEs at the ng/mL order of magnitude in water samples. The method offered high specific removing efficiency to trace levels of BDEs and ease of operation by magnetic separation. More importantly, the magnetic nanocomposites have stable chemical properties and good reusability, which can be reused at least 20 times.

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Author Contributions

Ning Gan design the main experimental scheme, idea and wrote most part of the paper, Jiabing Zhang and Shaichai Lin did all the chromatagraphia experiment and wrote part of the paper, Nengbing Long and Tianhua Li did all the characterization experiment. Yuting Cao design the part of the experimental scheme.

Conflicts of Interest

The authors declare no conflict of interest.

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