CQDs-Doped Magnetic Electrospun Nanofibers: Fluorescence Self-Display and Adsorption Removal of Mercury(II)

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ABSTRACT: This paper reports the carbon quantum dots-doped magnetic electrospinning nanofibers for the self-display and removal of Hg(II) ions from water. The fluorescent carbon quantum dots and magnetic Fe₃O₄ nanoparticles were pre-prepared successfully, and they appeared to be homogeneously dispersed in nanofibers via electrospinning. During the sorption of Hg(II) ions, the significant fluorescence signals of nanofibers gradually declined and exhibited a good linear relationship with cumulative adsorption capacity, which could be easily recorded by the photoluminescence spectra. The sorption performance of mercury ions onto the nanofibers was investigated in terms of different experimental factors including contact time, solution pH value, and initial ion concentration. Considering the actual parameters, the nanofibers were sensitive self-display adsorption system for Hg(II) ions in the existence of other cation. The sorption data were described by different kinetic models, which indicate that the whole sorption was controlled by chemical adsorption. The intraparticle diffusion mass transfer was not obvious in this system, which further proved the uniform adsorption and even fluorescence quenching in nanofibers. Additionally, the nanocomposite fiber could regenerate in several cycles with no significant loss of adsorption capacity and fluorescence intensity. Thus, the nanofibers are promising alternatives for environmental pollution incidents. It is especially competent due to its high efficiency for self-display and removal of high concentration of mercury ions.

1. INTRODUCTION

As one of the most challenging issues, heavy metal ion pollutants have evoked huge attention throughout the globe for many decades.1 In particular, the extremely toxic, mutagenic, and carcinogenic mercury (Hg) ions in the environment can cause a wide range of severe damage to the endocrine system, brain, kidneys, and even nervous system.2 They are often transformed into organic Hg(II) by bacteria and enter human body via the food chain with a high risk of bioaccumulation.3 Thus, the removal of mercury ions from the natural environment is significant owing to a matter of water safety, chemical analysis, and human health.4 Considerable new methodologies are accordingly being developed for effective recognition and removal of mercury ions. For example, several analytical tools to quantitatively trace Hg(II) ions have been reported, including atomic absorption spectroscopy,5 stripping voltammetric detection,6 neutron activation analysis,7 fluorescence detection,8 inductively coupled plasma (ICP) atomic emission spectroscopy,9 ICP-mass spectrometry,10 and cold vapor atomic fluorescence spectrometry.11 On the other hand, a wide range of absorbents, such as nanoparticles (NPs), metal–organic frameworks,12 natural polymers,13 porous silica,14 and hydrogels,15 are being considered for the possible adsorption to remove Hg(II) ions. To achieve adsorption and detection, to date, substantial bifunctional materials based on electrochemical, fluorescent, and optical probe have been designed, such as pillararene-based aggregation-induced-emission-active supramolecular,16 oligonucleotide-functionalized core/shell magnetic silica sphere@Au,17 magnetic self-assembled zeolite clusters,18 DNA-functionalized materials,4,15 magnetic cellulose–chitosan (CS) hydrogels,19 particulate ligand-impregnated nanomaterials,19–21 Fe₃O₄@SiO₂–Au@PSiO₂,22 thioether-based fluorescent covalent organic framework,23 cyclodextrin-modified magnetic NPs,24 rhodamine derivative functionalized CS,25 and luminescent gold NPs based materials.26,27 These assays provide a reliable and efficient indirect method for recognizing and removing Hg(II) ions. Nevertheless, most of the materials have a definite super-lower detection limit and an unmatched higher adsorption capacity. In other words, these composites are difficult to achieve continuous recognizable absorption, especially in the high mercury ion concentration.

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One-dimensional (1D) nanostructures have been arousing considerable interest due to their excellent performance and broad applications in many fields, such as drug carriers in controlled release, optoelectronics, food manufacturing, filtration, sensor technology, catalysis, and scaffolds in tissue engineering. Electrospinning provides a versatile and simple method for generating 1D nanofibers from an abundant variety of materials including synthetic and natural polymers, polymers loaded with chromophores, polymer alloys, active agents, metals, and ceramics. As a reliable and predictable approach, electrospinning can also used to effectively prepare a desirable fibrous membrane, which has an active laccase encapsulated inside and nanoscale channels distributed on the surface, and can be used for direct sorption of organic or inorganic contaminations from environmental water owing to their porous structures, high specific surface area, interconnectivity, and excellent mechanical properties.

Alternative materials derived from natural resources are innovative solutions to bring unprecedented advances for heavy metal adsorption applications. Agricultural wastes, chitin, alginate, starch, and gelatin were being developed as novel adsorbents due to their low cost and renewability. In particular, CS has been highlighted as a promising adsorbent because of its natural abundance, high surface activity, physicochemical robustness, biocompatibility, lightweight, low cost, and recyclability. However, it is difficult to achieve specific recognition and adsorption of Hg(II) ion when CS was applied as a metal-ion absorbent. Moreover, it is important to design customized adsorbents with the capacity of self-display, which aim to facile record the adsorption data, because of the commonly used and reliable technique for quantitatively assessing the absorption behavior of adsorbents is mainly based on gravimetric/volume determination. Such technologies are inefficient due to the lengthy and complex instruments required, which has limited its wide application in the adsorption process. Therefore, there is an urgent need to develop strategies for real-time noninvasive monitoring of Hg(II) ion absorption to minimize the uncontrollable parameters and intricate variability.

Herein, intrigued by the facile functionalization of 1D CS fibers, we propose a green material strategy for the development of real-time self-monitoring adsorbents that can address...
the aforementioned challenges. Specifically, we present a new class of porous adsorbents with synergistically coupled magnetic fluorescence bifunctionality. The adsorbents are composed of Fe₃O₄ and carbon quantum dots (CQDs)-functionalized poly(ethylene oxide) (PEO)/CS thin nonwovens. The NPs are evenly integrated with the PEO/CS nanoﬁbers by electrospinning technique (Figure 1). The CS molecules can readily coordinate with NPs to CS/NPs complexes due to their electron-rich amine groups in an array of π-conjugated geometries. The CQDs were used as ﬂuorescent probe for continuous and noninvasive monitoring of the adsorption of Hg(II) ions, which possess excellent photoluminescence (PL), high chemical stability, photostability, and zero toxicity. The Fe₃O₄ NPs were applied as synergistic adsorbent and magnetic function module. Furthermore, the magnetic ﬂuorescent nonwoven absorbent also holds great potential for applications in luminescent patterning, underwater ﬂuorescent devices, sensors, and biomaterials.

2. RESULTS AND DISCUSSION

2.1. Morphology of Fe₃O₄, CQDs, and Composite Nanoﬁber Membranes. The morphology of magnetic NPs, CQDs, PEO/CS, Fe₃O₄/PEO/CS, CQDs/PEO/CS, and Fe₃O₄/CQDs/PEO/CS composite nanoﬁber membranes were determined by transmission electron microscopy (TEM) analysis, whose results are shown in Figure 2. As seen, the CQDs exhibited an irregular surface and an average diameter of approximately 5 nm (Figure 2a). The Fe₃O₄ NPs were an approximately spherical particle with a size of 8 nm, which were evenly dispersed in aqueous solution (Figure 2b). The relatively smooth and uniform PEO/CS nanoﬁbers were fabricated on the collector with an average diameter of 102 nm and a length longer than 500 μm (Figure 2c). After incorporation of 4% Fe₃O₄ or 4% CQDs into the PEO/CS nanoﬁbers, the diameter of nanoﬁbers was slightly decreased to 95 or 98 nm, respectively. When two solid particles were added simultaneously at a total mass ratio of 8%, the diameter of nanoﬁbers was decreased to 61.1 nm. This can be explained by the increase in the electrical conductivity of electrospinning precursor solutions. The average diameter was slightly increased to 64.3 nm when the solid contents increased to 12%, which may be attributed to the uniform dispersion of solid particles and the formation of multiple-pore structures. Meanwhile, the nanoﬁber membranes exhibited a more smooth appearance and a more uniform diameter. When the particle content was higher than 12%, obvious particle protrusions emerged on the surface of the nanoﬁber membrane, and more branches appeared in one single nanoﬁber; thus, the homogeneity of nanoﬁbers was greatly reduced. This is potentially because the excessive Fe₃O₄/CQDs induced low viscosity and low interfacial tension of electrospinning precursor solutions. Figure S1 show the relationship between solution viscosity and the corresponding ﬁber diameter after adding different amounts of NPs, which indicated that the average diameter of nanoﬁbers increases with increase in viscosity. In addition, the Fe₃O₄ NPs play an important role in dispersing of CQDs because the particle distribution in Fe₃O₄/CQDs/PEO/CS nanoﬁbers is better than in CQDs/PEO/CS nanoﬁbers.

Figure 3a shows the degree of swelling of PEO/CS nanoﬁber membrane and its composites. As seen, the degree of swelling of the membranes was decreased after doping CQDs, which could be attributed to the formation of amide linkages between the free amino groups of CS and the carboxyl groups on the surface of CQDs, which were conﬁrmed via Fourier transform infrared (FT-IR) spectra in the ﬁgure. After composing Fe₃O₄, the degree of swelling further reduced, which could be explained by the electrostatic interaction between the magnetic particles and the CS molecular chain. These linkages can lead to adjacent ﬁber segments to fuse to each other, increase water diﬀusivity resistance, and decline the degree of swelling of composited nanoﬁbers, which was beneﬁcial to enhance the stability of the electrospinning membranes in the aqueous solution.
Figure 3b shows the XRD patterns of CQDs, Fe₃O₄, CS, PEO powders, PEO/CS, Fe₃O₄/PEO/CS, and Fe₃O₄/CQDs/PEO/CS composite fibers. As seen, the CQDs had a broad peak at 2θ = 26° assigned to the amorphous carbon structure, which was consistent with the previous reports. Because CS is a typical amorphous polymer, the XRD pattern of CS only had a significant discrete broad diffraction peak at 2θ = 20.8°, confirming that only Form II crystals are present in the chitosan powder. There were three diffraction peaks at 2θ = 19.4, 20, and 23.5° assigned to the characteristic peaks of CS and PEO. The diffraction peaks appearing in Fe₃O₄/PEO/CS at 2θ = 30.11, 35.41, 43.11, 53.41, 57.01, and 62.61° can correspond to the crystal planes of (220), (311), (400), (422), (511), and (440) of magnetite Fe₃O₄ (ICPDS11-0614), respectively. The characteristic diffraction peaks of CQDs was not present in the patterns of CQDs/PEO/CS and Fe₃O₄/CQDs/PEO/CS nanofibers, which indicated the good dispersion of CQDs in the nanocomposite.

To investigate the pore volume, pore diameter, and surface area of the nanofiber membranes, the Brunauer−Emmett−Teller (BET) adsorption/desorption isotherms (Figure 3c) were characterized. The pore-size distribution of different samples are demonstrated in Figure S2 and the corresponding surface texture characteristics are summarized in Table S1. All nanofibers exhibited typical type IV isotherms with an H₃-type hysteresis loop, which was the characteristic of mesoporous materials. As seen, both pristine Fe₃O₄ and CQDs exhibited a unimodal pore size distribution; however, the BET surface area of CQDs was slightly higher than that of Fe₃O₄ due to their amorphous carbon structure. Compared with the pristine PEO/CS fiber, the addition of Fe₃O₄ or CQDs could improve the specific surface area, average pore diameter, and pore volume. When the Fe₃O₄ and CQDs was added in the nanofibers simultaneously, the BET surface area increased from 32.281 to 38.234 m²g⁻¹. This indicated that the co-addition of magnetic materials and carbon materials produces a synergistic effect in improving the surface texture, which facilitated the improvement in physical adsorption abilities of the membranes.

The FT-IR spectra of Fe₃O₄, CQDs, PEO/CS, Fe₃O₄/PEO/CS, CS, PEO/CS, and Fe₃O₄/CQDs/PEO/CS composite fibers are exhibited in Figure 3d. As could be seen, the Fe₃O₄ spectrum exhibited the characteristic absorption peaks of Fe−O−Fe at 595 cm⁻¹. The CQDs spectrum manifested two obvious absorption peaks at 1710 and 1388 cm⁻¹, the former corresponded to the asymmetric vibrational peaks and symmetrical vibrational peaks of −COOH, which indicated that the carboxyl group was contained on the surface of the CQDs, whereas the latter corresponded to the −CH₂ group. In the spectrum of PEO/CS, the peak at 1635 cm⁻¹ was assigned to the deformation vibration of −NH₂, the broad band at 3200–3400 cm⁻¹ was attributed to the stretching vibration absorption band of N−H and O−H of the polysaccharide molecules, the absorption band at 1350–1460 cm⁻¹ was due to the vibration of −CH₂, the peak at 1635 cm⁻¹ was due to the C−C absorption band, and the broad band at ~1093 cm⁻¹ was associated with the C−O−C stretching vibration. These structures further confirmed the successive composition of CS and PEO. The FT-IR spectra of Fe₃O₄/CQDs/PEO/CS composite membrane maintained the characteristic peaks of Fe₃O₄ and CQDs without apparent migration, which indicated that Fe₃O₄ or CQDs are immobilized in nanofibers. In addition, minor peaks at 1630 and 1580 cm⁻¹ can be observed in CQDs/PEO/CS and Fe₃O₄/CQDs/PEO/CS composites, which can be attributed to the formation of amide linkages between the free amino groups of CS and the carbonyl groups on the surface of CQDs.⁴¹

Optical properties of samples were characterized via UV−vis diffuse-reflectance spectrum (UV−vis DRS) (Figure S3). The PEO and CS exhibited a strong sorption in the ultraviolet and near-ultraviolet region with a wavelength of less than 500 nm, which can be assigned to intrinsic absorption of CS and PEO molecular chains. The CQDs had two strong absorption bands, the peaks that occurred at 234−271 nm could be ascribed to π → π* transitions of aromatic rings and n → π* transitions of the C=O bonds; the minor peak at ~450 nm was probably due to the trapping of excited states from the surface states. The UV−vis DRS of Fe₃O₄, Fe₃O₄/PEO/CS, CQDs/PEO/CS, and Fe₃O₄/CQDs/PEO/CS exhibited similar absorption spectra profiles at 200−800 nm, which may contain the characteristic absorption range of polymer, CQDs, and/or magnetic materials.

Figure 4a shows the PL intensity of CQDs/PEO/CS and Fe₃O₄/CQDs/PEO/CS nanoﬁber membranes at excitation wavelengths of 420 nm with different solid particle contents (the corresponding fluorescence spectra are demonstrated in Figures S4 and S5, respectively). The CQDs/PEO/CS nanoﬁber membranes showed the excitation wavelength dependence similar to CQDs. With the increase in CQDs content from 4 to 16%, the fluorescence intensity of the nanofiber membranes first increased and then decreased, which may be attributed to the overall fluorescence intensity being relatively weak at low CQDs concentration, and a significant fluorescence quenching existed in the nanofibers at excessively high CQDs concentration. To investigate the effect of Fe₃O₄ on the fluorescence properties of CQDs, we studied the change in fluorescence intensity versus Fe₃O₄ contents. The fluorescence
intensity of the nanofiber membranes generally decreased after doping Fe3O4, which was partly due to the shielding effect of Fe3O4. However, the membranes with a lower CQDs content exhibited a higher sensitivity; the fluorescence intensity of membrane with 4% CQDs declined 62.5%, whereas that of the membrane with 8% CQDs declined 11.1%. This can be explained by the fact that the addition of Fe3O4 reduced the collision and fluorescence quenching in nanofibers. This phenomenon illustrated the dual effect of Fe3O4 on the fluorescence intensity of CQDs, which are the shielding and dispersion effects.

The magnetic properties of Fe3O4/PEO/CS and Fe3O4/CQDs/PEO/CS composite membranes are shown in Figure 4b. As could be seen, the magnetic composite membranes had almost immeasurable remanence and coercivity, which demonstrated their superparamagnetic behavior. With the increase in the addition amount of Fe3O4, the saturated magnetic strength of the composite nanofibers was approximately linearly increased, and the saturated magnetic intensity varied with Fe3O4 content as $y = 5.42013x + 0.5287$. When the Fe3O4 content increased to 8%, the saturation magnetic strength can reach 18.61 emu g$^{-1}$. In general, when the magnetic saturation magnetization reaches 16.3 emu g$^{-1}$, the magnetic material has the potential to be driven by permanent magnets, indicating that we have successfully fabricated a class of magnetically separable membranes.

To obtain the composition information of the nanofiber membranes and their thermal stability, we tested the thermogravimetric curves of the composite membranes containing different contents of CQDs and Fe3O4 NPs in the N2 atmosphere. As seen in Figure S6a, the weight loss of the PEO/CS nanofiber membranes near the 100°C is 3%, which could be ascribed to the decomposition of water on the surface of the nanofiber membranes. The second-stage weight loss platform was at 290−310 °C, with a weight loss of approximately 20%, which could be due to the decomposition of CS. The major weight loss of approximately 60% occurring at 310−450 °C could be assigned to the decomposition of PEO. The corresponding DTA curve showed two salient peaks at 293 and 427 °C, which corresponded to the maximum heat flow of CS and PEO in the exothermic process, respectively. As seen in Figure S6d, the four element hybridizations had several significant thermal decomposition platforms at 200−600 °C, the thermal decomposition materials included CQDs (200−600 °C), PEO (310−450 °C), and CS (290−310 °C). With the increase in CQDs/Fe3O4 contents from 8 to 16%, the weight loss rate gradually decreased from 73.6 to 66.1%; meanwhile, the mass of the residual material increased from 23.4 to 30.9%. In addition, after Fe3O4/CQDs composition, the decomposition peak of CS moved to a higher temperature, whereas the decomposition peak of PEO maintained its position, which indicates that some weak physical or chemical bonds may be formed between the NPs and CS. In general, the addition of Fe3O4/CQDs can improve the thermal stability of the nanofiber membranes, which was beneficial to realizing the commercialization of the absorbents.

2.2. Removal of Hg(II) Ions under Real-Time Fluorescence Monitoring. The effect of pH and Fe3O4/CQDs concentration on the Hg(II) ions sorption using Fe3O4/CQDs/PEO/CS nanofibers was investigated for the initial concentration of 100 mg L$^{-1}$, adsorbent dosage of 0.5 g L$^{-1}$, and temperature of 25 °C (Figure S7). As depicted, the Hg(II) sorption capacity decreased by increasing pH values from 3 to 8. At lower pH values, the amine groups on the adsorbent surfaces were easily protonated and positively charged, which resulted in an electrostatic repulsion of Hg(II) ions. Meanwhile, the competition between the Hg(II) ions and hydrogen ion in the solution for active adsorption sites was intensive. However,
at higher pH values, adsorbent surface was deprotonated and the presence of hydrogen ion in the solution decreased, which induced an increase in the adsorption amount of metal ions. Due to the low solubility of mercury hydroxide in an alkaline solution, it often formed an orange precipitate and further transformed to HgO state. When the pH values were higher than 7.0, the formation of the precipitate could decrease the adsorption capacity for Hg(II) ions. So, the maximum adsorption capacity was found at pH 7.0. The particle contents also have a non-negligible effect on the sorption efficiency (Figure S7) by increasing the Fe3O4/CQDs concentration up to 12%; further increase in Fe3O4/CQDs content can decrease the adsorption capacity of Hg(II) ions onto the Fe3O4/CQDs/PEO/CS nanofibers. Increase in the adsorption capacity could be attributed to the increase in the number of active sites on the nanofibers adsorbent due to the unique large surface, well-modified surface properties provided by NPs. Reduction in Hg(II) ions sorption at higher particle concentrations could be ascribed to the agglomeration of Fe3O4/CQDs. Thus, in the following study, a pH value of 7.0 and a solid particle content of 6% were chosen as research conditions.

The effect of contact time on the adsorption capacity of Hg(II) ions onto the Fe3O4/CQDs/PEO/CS composite nanofibers and their fluorescent quenching degree are shown in Figure 5b,c. As seen, the adsorption of mercury ions onto the adsorbent reached an equilibrium after only 100 min at the researched temperatures; 80% of the adsorption occurs in the first 60 min. This relationship of cumulative adsorption capacity and fluorescence quenching degree was established via linear fitting (Figure 5c); the relatively high integral regression correlation coefficients (R2 = 0.983) indicated the linear correlation between fluorescence intensity and the cumulative adsorption capacity. Moreover, the uniformity of the solid particle distribution exhibited a distinct facilitation effect on the fitting results. One can see that membrane 1 (6% Fe3O4 and 6% CQDs) shows the best linear fitting degree (R2 > 0.993) compared to membrane 2 (4% Fe3O4 and 4% CQDs) and membrane 3 (8% Fe3O4 and 8% CQDs). This can be explained by the fact that uneven distribution of CQDs can lead to irregular fluorescence quenching during the Hg(II) ion adsorption process. As reported, the CQDs can be employed as a sensitive and selective fluorescent probe for quantitative detection of Hg(II) ions, but they have a definite super-low detection limit around the nanomolar level. However, the as-prepared magnetic fluorescent nanofibers have the potential for real-time fluorescence, self-displaying the adsorption process even under high concentration of mercury ions. This is mainly attributed to the even distribution and homogeneous fluorescence quenching of CQDs in nanofibers. When Hg(II) ions gradually adsorb and diffuse into the interior of the nanofibers, the fluorescence of CQDs was gradually quenched, thus a certain relationship between the fluorescence intensity and the adsorption capacity of Hg(II) ions can be established.

The effect of competitive ions, including Ag(I), Zn(II), Cu(II), Cd(II), Fe(II), Ba(II), Pb(II), Mn(II), Ca(II), Mg(II), Cr(III), Fe(III), and Cr(VI), on the adsorption of Hg(II) ions was studied to confirm the selectivity of the fluorescence monitoring, whose results are shown in Figure 5d. The results proved that metal ions, such as Ag(I), Cr(VI), Pb(II), Cu(II), and Fe(III), could cause slight quenching, but to a relatively lower degree, whereas other metal ions had no obvious effect on the fluorescence intensity of nanofibers. These results indicated that the nanofibers were selective monitoring system for Hg(II) ions in the presence of other cations.

The application of detecting Hg(II) ion in real samples of rainwater was carried out by using an analogous procedure. The mercury concentration in the original rainwater samples was determined by ICP-AES to be 0.202 μg L−1, which is much lower than the ion concentration we added. Figure S8 exhibits the photos of membrane 1 under UV excitation (420 nm) at different adsorption times. As seen, the fluorescence intensity of the nanofiber membranes decreased gradually with increase in the adsorption time, and the fluorescence was almost...
completely quenched at about 150 min. This could be because when the mercury ions gradually mass-transferred toward the interior of the nanofibers, the mercury ions could bind to the surface of the CQDs at different positions until all CQDs inside the nanofibers were completely quenched. The linear fitting results (Figure S9) showed the fluorescence intensity had a good linear correlation with the cumulative adsorption capacity in rainwater ($R^2 = 0.992$), which indicated that these nanofiber membranes could be extensively applied in actual activities.

2.3. Equilibrium, Kinetics, and Thermodynamics. The sorption capacity of nanofibers versus the initial concentration of Hg(II) ions and temperatures are shown in Figure 6a. The equilibrium data of Hg(II) ions adsorption onto the Fe$_3$O$_4$/CQDs/PEO/CS nanofibers were described via Langmuir and Freundlich isotherm models. The parameters of isotherm models, which were calculated via linear regression, are shown in Figure 6b−d and summarized in Table S2. As seen, the Langmuir isotherm model ($R^2 > 0.994$) was more suitable than Freundlich ($R^2 > 0.958$) isotherm model to describe the equilibrium data. This behavior suggested the monolayer adsorption process of Hg(II) ions onto Fe$_3$O$_4$/CQDs/PEO/CS nanofibers. Thermodynamic parameters including enthalpy change ($\Delta H$), entropy change ($\Delta S$), and Gibbs free energy change ($\Delta G$) usually play a vital role in determining the degrees of feasibility and spontaneity of the sorption process. $\Delta G$ of the adsorption process can be reckoned by eqs 1 and 2.

$$\Delta G = -RT \ln k_c$$

$$k_c = \lim_{c_l \to 0} \frac{C_s}{C_d}$$

where $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is an absolute temperature (K), and $k_c$ is the adsorption equilibrium constant, and $C_s$ and $C_d$ are the values of solid and liquid phase concentration (mg L$^{-1}$), respectively. The relationship between the equilibrium constant ($k_c$) and the temperature can be calculated by the Van’t Hoff equation (eq 3).

$$\ln k_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

The values of $\Delta S$ and $\Delta H$ can be obtained from the slope and intercept of the Van’t Hoff plot of $\ln k_c$ versus $1/T$ (Figure 6d). The thermodynamic parameters are summarized in Table S3. The endothermic and spontaneous features of mercury ions adsorption onto the nanofibrous adsorbent could be confirmed by the positive values of $\Delta H$ and negative values of $\Delta G$. Furthermore, the positive values of $\Delta S$ indicated the increased randomness at the solid−solution interface.

The typical pseudo-first-order and pseudo-second-order kinetic models and intraparticle diffusion models were applied to describe the kinetic data of Hg(II) ions onto the Fe$_3$O$_4$/CQDs/PEO/CS nanofiber adsorbent (6% CQDs and 6% Fe$_3$O$_4$) in Figure 5b. The linear fitting results are presented in Figure 7a−c and Table S3. As shown, the pseudo-second-order kinetic model ($R^2 > 0.993$) could well describe the kinetic data of Hg(II) ions adsorbed by the Fe$_3$O$_4$/CQDs/PEO/CS nanofibers compared with pseudo-first-order kinetic model ($R^2 > 0.980$) and intraparticle diffusion models ($R^2 > 0.980$). This indicated that the adsorption was a rapid process, which was mainly controlled by chemical adsorption. Furthermore, the intraparticle diffusion mass transfer resistance was not obvious in this system, which further proved the uniform adsorption and even fluorescence quenching in nanofibers.

Under optimum conditions, the adsorption capacity of CQDs, Fe$_3$O$_4$/PEO/CS, CQDs/PEO/CS, and Fe$_3$O$_4$/CQDs/PEO/CS adsorbents for Hg(II) ions was determined. The results exhibited that the maximum experimental adsorption capacity of Hg(II) ions onto different adsorbents was in order Fe$_3$O$_4$/CQDs/PEO/CS (108 mg g$^{-1}$) > Fe$_3$O$_4$/PEO/CS (94 mg g$^{-1}$) > CQDs/PEO/CS (88 mg g$^{-1}$) > CS (79 mg g$^{-1}$) nanofibrous adsorbents. Therefore, the composition of CQDs and Fe$_3$O$_4$ has a synergistic effect on the enhancement of sorption capacity to the nanofibrous adsorbents. The results of five cycles of adsorption/desorption of Hg(II) ions onto the Fe$_3$O$_4$/CQDs/PEO/CS nanofibrous adsorbent is illustrated in Figure 7d, which showed that the Fe$_3$O$_4$/CQDs/
PEO/CS nanofibrous adsorbent can be reused frequently without significant loss in fluorescence intensity and sorption capacity. After five cycles, the saturated adsorption capacity of mercury ions decreased by 12.4% and the fluorescence intensity decreased by 12.9%. The possible reason was the erosion of the active adsorption sites by HNO₃ and the change in the surface structure of CQDs, respectively.

3. CONCLUSIONS

A magnetic fluorescence nanofiber membrane had been strategically prepared by immobilizing CQDs and Fe₃O₄ into PEO/CS nanofibers via electrospinning to effectively remove the mercury ions existing in water. The nanofibers membrane exhibited a high adsorption efficiency for the mercury ions as the synergistic effects of polymer materials and inorganic nanoparticles. The mercury ions’ sorption achieved an equilibrium within 100 min and the maximum monolayer sorption capacity was 148.148 mg g⁻¹. On the basis of the good linear relationship between the adsorption capacity of mercury ions and the fluorescence intensity of membranes, we developed a facile method for real-time and noninvasively tracking of adsorption. The results of equilibrium, kinetics, and thermodynamics experiment indicated that adsorption was a rapid process and mainly controlled by chemisorption. The presence of Fe₃O₄ in the membrane also facilitates the separation of the nonwoven membrane from the solution, thus this nonwoven membrane has a great potential for the application in actual wastewater.

4. METHODS

4.1. Instruments and Analyses. The N₂ adsorption/desorption isotherms were conducted via Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda pore-size distribution analyzer (Quantachrome NOVA-4000e) at 77 K. The TEM images were obtained using a high-resolution transmission electron microscopy (HRTEM, TECNAI G2 F20) and operated at the accelerating voltage of the electron beam of 200 kV. The diameter distributions and the average diameters of nanofibers were measured via an image analyzer (Image-Proplus, Media Cybernetics). Thermogravimetric analysis was conducted under a nitrogen atmosphere flow at a heating rate of 10 °C min⁻¹ (NETZSCH STA 409/PC). The magnetic properties were measured on a 7407 vibrating sample magnetometer (Lakeshore Instrument Plant) in the range of −15 000−15 000 Oe at room temperature. The PL spectra data were determined using a steady-state Hitachi F-7000 fluorescence spectrometer; the excitation wavelength was selected at 320−500 nm. The FT-IR spectra were recorded on a Spectrum Two FT-IR spectrometer (Perkin-Elmer) in the range of 200−4000 cm⁻¹ with 4 scans. The UV−vis DRS were determined on a U-3900 spectrometer with a D2 (deuterium) lamp for the ultraviolet range and a WI (halogen) lamp for the visible and near-infrared regions, respectively.

4.2. Synthesis of CQDs and Fe₃O₄ NPs. The CQDs were fabricated via thermal treatment of Val according to a method reported earlier. The general procedure is exhibited as follows: 1 mL aqueous Val solution (100 mg mL⁻¹) and 2 mL concentrated phosphoric acid were mixed and heated for 4 h at 90 °C. The obtained brown solution was neutralized to pH 7 using 1 M NaOH solution and filtered through a 0.45 μm polyethersulphone membrane to remove insoluble particles. The CQDs were further purified via dialyzing against deionized water (MWCO 1 kDa) for 48 h. The Fe₃O₄ NPs were synthesized by a reported high-gravity reactive precipitation method by intense microscopic mixing of NaOH, FeCl₃, and FeCl₂ at 80 °C. Briefly, FeCl₂ and FeCl₃ were dissolved in deionized water at a molar ratio of 1:2, and then the obtained solution was chemically precipitated by 30% NaOH solution in impact stream-rotating packed bed under the protection of nitrogen. The suspension was separated using a magnet and washed several times using ethanol and deionized water until the pH value of the filtrate was neutral.

4.3. Preparation of Nanocomposite Fibers. The preparation process of magnetic fluorescent nonwovens was showed as follow; first, CS and PEO (w/w = 1:1) were dissolved in the mixed solvent of water and acetic acid (v/v = 1:1) to obtain a mixed solution with a solid concentration of 5%. After stirring for 24 h, the CQDs and Fe₃O₄ were dispersed in the transparent solution at a mass ratio of 1:1 and then the mixture was stirred for another 2 h to obtain a brown uniform solution. After standing and defoaming for 24 h, the solution was loaded into a 5 mL plastic syringe equipped with a syringe needle of 0.9 mm inner diameter. The nanofibers membrane with magnetic fluorescence properties was prepared via electrospinning (TEADFS-100+, Beijing Technova Technology Co., Ltd, China) at a voltage of 22 kV, a tip-collector distance of 10 cm, a feeding rate of 0.5 mL h⁻¹, and an air humidity less than 10% at room temperature. The prepared nanofiber membranes were stored in a vacuum oven before use. For comparisons, the spinning solution without the solid particles or with only one kind of particles is also configured for electrospinning.

4.4. Swelling Studies of Nanofiber Membranes. To discuss the stability of composite nanofiber membranes in an aqueous solution, the degree of swelling was investigated on the PEO/CS-based nanofiber membranes. Typically, dry membranes were immersed in 25 °C deionized water for 24 h. The experiments continued until the weight of the membranes generally remained stable. The degree of swelling was calculated expressed as the masses increase versus the mass of dried nanofibers.

4.5. Real-Time Fluorescence Monitored Adsorption Experiment. The pre-prepared PEO/CS, Fe₃O₄/PEO/CS, CQDs/PEO/CS, and Fe₃O₄/CQDs/PEO/CS nanofibers were applied as adsorbents for the removal of Hg(II) ions from the aqueous system. All batch sorption experiments were performed on a model THZ-82A (Shaker) (Jiangsu Kexi Instrument Co., Ltd, China) with a shaking speed of 200 rpm. The concentration of mercury ions in the solution was determined by ICP-AES (Model ICAP 9000, Jarrell-Ash). The sorption capacity of the metal ions adsorbed onto each adsorbent was calculated via following equation.
\[ q \ (mg/g) = \frac{(c_0 - c_e)V}{W} \]  

(4)

where \( c_0 \) and \( c_e \) are the initial and equilibrium concentrations of the Hg(II) ions in the testing solution (mg L\(^{-1}\)), \( V \) is the volume of the testing solution (L), and \( W \) is the mass of the adsorbent (g). The adsorption kinetics of the Hg(II) ions onto the nanofibers were determined with an initial concentration of 100 mg L\(^{-1}\), pH values of 2–7, a temperature of 25 °C, and lasted for 150 min. Meanwhile, the PL spectra data of different membranes during adsorption were recorded at an excitation wavelength of 420 nm after rapid magnetic separation. The selectivity was confirmed by adding other analogues, including Ag(I), Zn(II), Cu(II), Cd(II), Fe(II), Ba(II), Pb(II), Mn(II), Ca(II), Mg(II), Cr(III), Fe(III), and Cr(VI) instead of Hg(II) after 150 min adsorption. Pseudo-first-order\(^{46,47}\) and pseudo-second-order kinetic\(^{48}\) and intraparticle diffusion models\(^{49,50}\) were employed to analyze the sorption data (eqs 5–7).

\[ q_t = q_e(1 - \exp(-k_1t)) \]  

(5)

\[ q_t = \frac{k_2q_e^2t}{1 + k_2q_e t} \]  

(6)

\[ q_t = k_3t^{1/2} + C \]  

(7)

where \( q_e \) and \( q_t \) (both mg g\(^{-1}\)) are the sorption capacity at equilibrium time and time \( t \), respectively; \( k_1 \) (min\(^{-1}\)), \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)), and \( k_3 \) (mg g\(^{-1}\) min\(^{-1}\)) are the pseudo-first-order, pseudo-second-order, and intraparticle diffusion sorption rate constants, respectively; and \( C \) is the intraparticle diffusion adsorption constant.

The adsorption isotherm experiment was carried out with different initial concentrations (10–200 mg L\(^{-1}\)), contact time (0–150 min), and temperature (25–45 °C). Acetic acid (0.1 M) or NaOH were used to adjust the pH value. Freundlich and Langmuir isotherm models\(^{40,46} \) (eqs 8 and 9) were applied to analyze the equilibrium data.

\[ q = k_{nL}q_e^{1/n} \]  

(8)

\[ q = \frac{q_m}{1 + K_eq_e} \]  

(9)

where \( K_q \) is the Langmuir equilibrium constant, \( k_p \) and \( n \) are the Freundlich equilibrium constants, and \( q_m \) is the maximum sorption capacity. For the regeneration of the nanofiber membranes, the nanofibers were washed with 1 mol L\(^{-1}\) HNO\(_3\), 1 mM EDTA, and then washed several times with deionized water. The adsorption/desorption cycle was repeated four times using the same nanofiber membranes.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01969.

Relationship of the viscosity of the spinning solution and average diameters of nanofibers; pore-size distribution of different samples; textural characteristics of the samples; UV–vis diffuse reflectance spectroscopy of different samples; PL spectra of different samples with different excitation wavelength; thermogravimetry and differential thermogravimetry curves of electrospun nanofiber membranes with different content; effect of pH values and particle contents on equilibrium adsorption capacity; the photos of membrane 1 under UV excitation (420 nm) at different adsorption time; comparison of fluorescence detection and ICP-AES results in real rainwater samples; kinetic parameters of Hg(II) ions adsorption onto the Fe\(_3\)O\(_4\)/CQDs/PEO/CS nanofibrous adsorbent; isotherm parameters and thermodynamic parameters for Hg(II) sorption onto the Fe\(_3\)O\(_4\)/CQDs/PEO/CS nanofibrous adsorbent (PDF)

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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**Notes**

The authors declare no competing financial interest.

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