Facile fabrication of nanocomposites by modified carbon black loading with magnetite nanoparticles for fast removal of cadmium ions

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Abstract

Magnetic nanomaterials have unique advantages in heavy metal ions absorption because of their large specific surface area and easy magnetic manipulation. Carbon nanotube or graphene loaded with magnetite nanoparticles (MNP) have been utilized to fabricate absorbents with both high absorption capacity and fast magnetic capture. Herein, cheap commercial carbon black was used as a substitute for expensive carbon nanotube or graphene to fabricate nanocomposites (CB-MNP) by modified carbon black loaded with superparamagnetic MNPs. The fabrication process is accomplished by two steps. Carbon blacks (CB) were modified by nitric acid to produce a large number of carboxyl groups on the surface and make stable aqueous dispersion. Subsequently, CB-MNPs with high water stability and fast magnetic response were facilely prepared by iron precursors (the ratio of ferrous to ferric is 1:2) added into the above CB dispersion and tuned pH = 10, finally added polyacrylic acid solution under sonication. Modified CB and CB-MNPs were characterized by transmission electron microscope (TEM), dynamic laser scattering (DLS), thermogravimetric analysis and so on. Water stability and magnetic response can be controlled by changing the proportion of CB and iron precursor. As a proof-of-concept, CB-MNPs were used for absorption removal of cadmium ions. Excellent performance was demonstrated with the removal efficiency of 71.41% and removal capacity of 39.99 mg·g⁻¹ at the initial concentration of Cd²⁺ as 5 × 10⁻⁵ mol·l⁻¹. The effects of initial concentration of Cd²⁺, pH value and interfering anion ions were also investigated and the results indicate the potential application of CB-MNP in fast removal of heavy metal ions.

1. Introduction

Heavy metal ions have strong toxicity to human beings and other organisms, some of which do harm to human health even in a very small concentration [1]. Effective removal of heavy metal ions in waste water has attracted rising attention because these have caused serious environmental problems [2]. Many approaches such as chemical precipitation, adsorption, oxidation-reduction, evaporation, ionic exchange, electrochemical treatment, and membrane separation techniques have been developed for the removal of heavy metals from wastewaters [3–6].

Adsorption technique is considered the most attractive technique because it is easy to operate and recycle [5]. The key to remove heavy metal ions from water by adsorption is the preparation and optimization of adsorption materials. Traditional adsorption materials such as clay, oxide, molecular sieve and activated carbon have been used to remove heavy metal ions [7–9]. However, many materials are limited in application due to their low adsorption efficiency, poor chemical stability and difficulty in recycling. Nano materials as adsorbents have unique advantages because their specific surface area increases rapidly with the decrease of particle size [10–12]. Several kinds of nano materials such as nano zero valent iron, iron oxide, titanium dioxide have been utilized for...
After absorbing heavy metal ions, most nano materials require extra centrifugation, filtration and other steps to separate them from water, which is inconvenient to operate. Therefore, nano materials such as superparamagnetic nanoparticles have unique advantages in heavy metal ions absorption because of their large specific surface area and easy magnetic manipulation [17, 20]. The former brings a high absorption capacity of heavy metal ions and the latter provides a fast capture for the isolation. Moreover, they can be repeated capture and disperse many times under the presence and absence of external magnetic field. Theoretically, magnetic nanoparticles with smaller particle size have larger specific surface area and achieve higher adsorption capacity. Actually, the particles with too small size are of extremely weak magnetic response and large size sacrifice specific surface area. It is very difficult for single nanoparticles to realize both of the above-mentioned advantages.

In order to fabrication of heavy metal ion absorbents owing both of large specific surface area and easy to be collected by magnet, carbon nanotubes or graphene have been selected as carrier to load with superparamagnetic nanoparticles [21–29]. Carbon nanotubes or graphene not only have high specific surface area but also can be chemically modified to have functional groups like carboxyl and amino on their surface, which make them easy to load nanoparticles [30–32] and adsorb heavy metal ions. Nanocomposites formed by modified carbon nanotube or graphene loading with superparamagnetic nanoparticles are of large specific surface area and easy magnetic manipulation and have special merits over single magnetic nanoparticles [33–35]. These nanocomposites have been successfully utilized for fast removal of heavy metal ions or organic wastes from water. However, carbon nanotubes or graphene are expensive, which limits their larger scale application in industry. Inspired by the facile fabrication of nanocomposites, graphene loading with Fe3O4 nanoparticles, through coprecipitation method [30–32]. Herein, we used cheap carbon black as a substitute for expensive carbon nanotubes or graphene to fabricate nanocomposites by modified carbon black loading with superparamagnetic nanoparticles for fast removal of heavy metal ions. Hydrophobic carbon blacks were chemically modified to be hydrophillic and then loaded with magnetite nanoparticles by coprecipitation of Fe2+ and Fe3+ under basic conditions (scheme 1). The stability of modified carbon blacks and their nanocomposites (carbon black loaded with superparamagnetic magnetite nanoparticles, CB-MNP) were investigated. The absorption performance of CB-MNP was also evaluated. To our best knowledge, carbon black is the first to be used as carrier loading with Fe3O4 nanoparticles. Lower cost of carbon black than carbon nanotubes or graphene as carrier to load nanoparticles facilitate to application in industry.

### 2. Experimental

#### 2.1. Materials

Carbon black, non-hydrophillic, purchased from Tianjing Lihuajin Chemical Engineering Co., Ltd; Nitric acid, Ferrous sulfate heptahydrate (FeSO4·7H2O), ferric sulfate (Fe2(SO4)3), Cadmium nitrate, ammonia, purchased from Xilong Chemical Co., Ltd; polyacrylic acid (PAA), Triaminopropionic acid, purchased from aladdin.
2.2. Procedures

2.2.1. Modification of carbon black
In a typical synthesis, 0.170 g of carbon black was dispersed in 10 ml of nitric acid by the aid of ultrasonic. The dispersion was then transferred into a Teflon lined stainless-steel autoclave (20 ml capacity) and heated at 100 °C for 3 h. After cooling down to room temperature, black colloidal dispersion was poured into one beaker and tuned pH to neutral. The modified carbon black precipitate was obtained after five times of centrifugal separation and water washing. The above precipitate was dissolved in 10 ml of water to make aqueous dispersion or directly dried at vacuum to get about 0.1 g of solid samples. The concentration of carbon black dispersion was determined by weighing the vacuum dried precipitate that centrifugal separation from 5 ml of dispersion. The final black dispersion was diluted to 2 mg • ml⁻¹. The procedures for syntheses of other samples are similar but change the temperature, amount of nitric acid and reaction time.

2.2.2. Synthesis of CB-MNP
In a typical synthesis, 0.4 g (0.1 mmol) of Fe₂(SO₄)₃, 0.2780 g (0.1 mmol) of FeSO₄·7H₂O and 2 ml of the above carbon black dispersion (2 mg • ml⁻¹) were mixed in 20 ml of distilled water. The mixed solution was adjusted pH = 10 by ammonia under the sonication. Subsequently, 10 ml of PAA solution with a concentration of 0.14 mol • l⁻¹ was added into the above black solution and kept sonication 3 min more. Finally, the black sediment was separated magnetically and washed with deionized water several times to eliminate organic and inorganic impurities, and then redispersed in 10 ml of deionized water. The procedure for determination of the concentration is similar to that of carbon black and the final concentration of CB-MNP was set as 2 mg • ml⁻¹. The solid sample was obtained by dried in a vacuum at 60 °C for 6 h. The procedures for syntheses of other samples are similar but change the amount of PAA, carbon black and the concentration of iron precursors.

2.2.3. Absorption of cadmium ions
In a typical adsorption procedure, 200 μl of CB-MNP dispersion was added into centrifuge tubes containing 20 ml of cadmium ions with concentration of 0.5 • 10⁻⁵ mol • ml⁻¹ (5.6 mg l⁻¹) or 1 • 10⁻⁴ mol•ml⁻¹ (11.2 mg • l⁻¹). The tubes were then shaken (100 rpm) at 25 °C. In order to get absorption equilibrium time and capacity, every 1 ml of the mixture was taken at different time intervals such as 1, 2, 5, 10, 30, 60, 120 and 180 min. The concentration of cadmium ions was determined by ICP after removal of CB-MNP by magnet and filtered through 0.22 μm filter membrane. The influences of pH conditions (pH = 3, 4, 5, 6, 7, 8, 9, 10) and cation ions (NaCl, NaSO₄, Na₂CO₃ and Na₃PO₄) on the absorption performance were also evaluated by similar procedures. The absorption capacity was calculated by the following equation:

\[ q_e = \frac{(C_0 - C_e) V}{V_1 C_1} \]

Where \( C_0 \) (mg • l⁻¹) is the initial concentration of cadmium ions; \( C_e \) (mg • l⁻¹) is the equilibrium concentration; \( V \) (ml) is the volume of cadmium ions; \( C_1 \) is the concentration of CB-MNP; \( V_1 \) is the volume of CB-MNP.

2.3. Characterization

TEM observation (TEM, JEOL 2010F) was used for observing the size and morphology of the magnetite NPs. Hydrodynamic size was measured on Malvern nanosizer A90. X-ray diffraction (XRD) was recorded on PANalytical Xpert Pro with Cu Kα radiation (1.540 56 Å) at 40 kV, 40 mA to confirm the nanocrystal phase and particle size. Raman spectra were obtained by Renishaw invia Raman microscope using a laser at 532 nm. TGA was measured by a Netzsch STA449C theromgravimetric analyzer (heating solid powders from 30 °C to 1000 °C at 15 °C min⁻¹ under a nitrogen flow). Magnetization of CB-MNP was carried out on a Lakeshore 7400 vibration sample magnetometer (VSM). Cadmium concentrations were determined by inductively coupled plasma emission spectroscopy (ICP, ICA P6300, Thermo Fisher, USA).

3. Results and discussion

3.1. Hydrodynamic size analysis and stability of modified carbon black
There are a large number of unsaturated bond (c=c) in carbon nanotubes and graphene, which make them easily oxidized to produce a large number of hydrophillic groups on the surface. For example, the modification of carbon nanotubes [36] and graphene [37] through oxidation agents like nitric acid lead to a large number of carboxyl groups on the surface, which endow them with high water stability. Herein, several modified carbon black samples with high water stability were prepared by setting different temperature and added different volume of nitric acid. We marked the samples as CB-N**-T***. For example, CB-N12-T80 means that the volume of nitric acid is 12 ml and the temperature is 80 °C in the reaction. As shown in figure 1(a), setting temperature as...
80 °C and changing the added volume of nitric acid as 8, 10 and 12 ml, respectively, three modified CB samples show two distribution peaks and the average sizes are over 200 nm. Also, they are not stable and deposit completely after 30 min as shown in figure S1 is available online at stacks.iop.org/NANOX/1/010052/mmedia. Setting temperature as 100 °C (figure 1(b)) and 120 °C (figure 1(c)) and changing the added volume of nitric acid as 8, 10 and 12 ml, all of six modified CB samples show single distribution peaks and the average sizes do not have significant change with the different added volume of nitric acid. Their aqueous dispersion are stable and have no obvious precipitates observed after 30 min (figure S2). Figure 1(d) exhibits the size distributions of modified CB samples prepared by fixed the same added volume of nitric acid as 12 ml and setting different temperature as 80 °C, 100 °C and 120 °C. The hydrodynamic sizes decrease with the increase of the added volume of nitric acid. These results reveal that 100 °C for oxidation of CB by nitric acid is required to produce enough carboxyl groups, which allows for modified CB with high water stability. The sizes of modified CB can be tuned by temperature but not by nitric acid.

Generally, colloidal stability results from one or both interactions of interparticle electrostatic or steric repulsion. To explore the mechanism of water stability, we further investigated the water stability under different pH value. As shown in figure S3 (pH = 5, 7 and 8), CB-N12-100 will soon produce precipitates at pH = 5 and remain stable at pH = 7 and 8 even after kept for 24 h. Zeta potential at pH = 5, 7 and 8 are measured and given the values as −8.6 mV, −38.3 mV and −43.5 mV, respectively. The value of pH = 5 is close to isoelectric point (pH ≈ 4) of carboxyl groups so that CB-N12-10 has low charges on the surface and is easy to deposit. Therefore, interparticle electrostatic repulsion mainly accounts for the water stability of modified carbon black, which facilitates to the application of modified carbon black in heavy metal ions absorption and removal.

To further investigate the water stability of modified carbon black, we measured the hydrodynamic size of CB-N12-T100 at different time. Figure 2(a) shows the particle size distribution of carbon black dispersion at different times and figure 2(b) exhibits the variation of average particle size with time. As shown in figure 2(a), the size distribution by volume is also unimodal and no marked large. The average size just fluctuates at 140 nm ± 3 nm. These results indicate that the modified carbon black are stable in neutral water dispersion.

3.2. Characterization of CB-MNP nanocomposites
CB-MNP nanocomposites (CB loaded with magnetite nanoparticles) were in situ fabricated by CB mixed with Fe^{2+} and Fe^{3+} under basic conditions. Four samples marked as CB-MNP-0.5, CB-MNP-1.0, CB-MNP-2.0 and
CB-MNP-3.0 were prepared by added different volume of CB dispersion, where MNP is magnetite nanoparticles and the values of 0.5, 1.0, 2.0 and 3.0 correspond to the added volume of carbon black dispersion. For comparison, we also prepared the MNPs under the same procedure except absence of the CB as the synthesis of CB-MNP.

TEM image of MNPs and its size distribution are shown in figures 3 (a) and (b). MNPs are dispersed individually on the copper grid. High resolution TEM image (the inset in figure 2(a)) of MNPs show that they are single nanocrystals and random analysis of 200 particles in figure 3(a) gives the average size as 7.2 nm (figure 3(b)). Figure 3(c) shows the TEM image of modified carbon black. The morphology of carbon black microparticles is irregular. The size of the microparticles can not be estimated from TEM image because they agglomerate or overlap on the copper grid sheet. Figure 3(d) show the TEM image of CB-MNP-2.0. A large number of nanoparticles loaded on the carbon black surface. The average size of the nanoparticles is 7 ± 2 nm. High resolution TEM image (figure 3(e)) enlarged from white circle area of figure 3(d) indicates that nanoparticles are single crystals and show different direction of lattice, which means they are randomly loaded on the surface of CB. As shown in the inset of figure 3(e), there is a value of 0.253 nm between two adjacent lattices corresponds to the lattice spacing of (311) planes of cubic magnetite [38]. It can be seen CB as carrier in figure 3(d) and amorphous CB in the edge of particles, which testify that MNPs are loaded on the surface of the CB. Selected area electron diffraction (SAED) pattern from enlarged black circle area of figure 3(d) is recorded in figure 3(f). The diffraction circles formed by discontinuous spots reveal the single-crystal-like pattern. Each radius of diffraction circles equals to its crystal lattice spacing. We carefully measured the length of the scale (s)
and the diameter of the diffraction scale (x) and calculate the crystal lattice spacing (d) according to the equation
\[ s/(10\text{ nm}) = x/(2d) \]
The lattice planes corresponding to the values of lattice spacing are listed in figure 3(f), which match with the reported results [39], suggesting that a large number of nanocrystals are randomly loaded on the CB’s surface.

The XRD patterns for MNP and CB-MNP-2.0 are presented in figure 4(a). CB are amorphous so that it is of no diffraction peaks. Both of MNP and CB-MNP-2.0 have similar diffraction patterns. The peaks at 2\(\theta\) = 30.1°, 35.4°, 43.1°, 53.4°, 57.1° and 62.6° can be indexed to (220), (311), (400), (422), (511) and (440) lattice planes of cubic magnetite, respectively (JCPDS 19-629). Approximately 7.5 nm of the average crystallite size is calculated from the XRD pattern (311) according to Scherrer equation. The results match with the analyses of TEM, HRTEM and SAED.

In order to get more exact average particle size by the Scherrer formula from broaden diffraction patterns, low scanning speed is required during the measurement of nanocrystals. Figure 4(b) shows the diffraction patterns between 32° and 46° at a scanning step of 1° min \(^{-1}\). All four samples and MNP have the same average crystal size (7.5 ± 0.3 nm) calculated from (311) planes according to Scherrer equation. MNP and four CB-MNP samples have the same average size revealing that CB has no influence on the particle size of MNPs.

Raman spectroscopy is an important tool for the characterization of the different carbon allotropes such as carbon nanotubes, graphite, graphene, carbon black, etc. Also, it can be utilized to further distinguish crystal phase between Fe₃O₄ and γ-Fe₂O₃ nanoparticles, which have the same inverse spinel structure and similar XRD patterns at nanometer scale. According to the reported results, there are three peaks around 350, 500 and 700 cm\(^{-1}\) for γ-Fe₂O₃ while Fe₃O₄ just has one peak near 667 cm\(^{-1}\) [40, 41]. The Raman spectrum of MNP is recorded at figure 4(c) and CB and CB-MNP-2.0 are shown in figure 4(d). Only one peak at 685 cm\(^{-1}\) is appeared between 200 and 700 cm\(^{-1}\) in figure 2(c). Raman spectrum for CB-MNP-2.0 has a similar peak at 685 cm\(^{-1}\) in figure 2(d). These results indicate that the crystal is Fe₃O₄. The CB show two typical peaks at 1345 and 1588 cm\(^{-1}\), corresponding to the D’s band and G’s band, respectively [42]. The results match with amorphous CB. The composite CB-MNP-2.0 appeared two peaks at 1380 and 1564 cm\(^{-1}\), which are broader than those in CB and the D’ band shift from 1345 cm\(^{-1}\) to 1380 cm\(^{-1}\) and the G’s band from 1588 cm\(^{-1}\) to 1564 cm\(^{-1}\). As shown in figure 4(c), MNP’s spectrum have two peaks at 1378 and 1578 cm\(^{-1}\), which corresponding to –CH₂– and C=O mode in the PAA.

Figure 4. (a) XRD patterns of MNP and CB-MNP-2.0 recorded at the scanning step 5°/min; (b) XRD patterns of MNP and four CB-MNP samples recorded at the scanning step as 1°/min; (c) and (d) Raman spectra of MNP, CB and CB-MNP-2.0.
Therefore, the peak shift for CB can be attributed to the overlapped Raman absorption of C=O and –CH2− in PAA on the surface of the magnetite nanoparticles.

Figure 5(a) shows the hydrodynamic size of the pure MNPs and modified CB. The size distribution of MNPs and CB are mono peak, indicating they are stable and no aggregation in water. The average hydrodynamic size of MNPs and CB are 28 nm and 130 nm, respectively. The MNPs are well dispersed in water at pH > 4.5 and can be deposited and magnetic separated at pH < 4, revealing that the surface of MNPs are coated with PAA. In spite of owning much larger size than MNPs, modified CB are also stable at pH > 6. Zeta potential varying with pH are shown in figure 5(b). There is a similar isoelectric point around pH = 4 for all three samples of MNPs, CB and CB-MNP-3.0, which indicate that there are a large number of carboxyl groups on the surface. A large number of carboxyl groups with negative charges produce interparticle electrostatic repulsion which make MNPs, CB and CB-MNP with high water stability. The hydrodynamic size of four CB-MNP samples are exhibited in figure 5(c). The average hydrodynamic size for four samples are 432 nm, 280 nm, 235 nm and 206 nm, respectively. The size decrease with the increase of the added volume of carbon black dispersion as shown in figure 5(d). Kept the amount of iron precursor fixed in the synthesis process, increasing the proportion of CB means that one carbon black particle loaded with less MNPs. As expected, the size of CB-MNP can be tuned by the ratio of CB added and higher ratio of CB leads to large particle size.

To investigate the organic species on the surface of the nanocomposite, TGA curves were recorded from 30 to 800 °C as shown in figure 6. Total weight loss for CB before modified is 7.0% and CB after modified is 33.8%. Generally, organic species can not be decomposed below 200 °C so that the weight loss at this temperature range is attributed to residue free or bounded water. Deducted weight loss below 200 °C for CB before modified 2.1% and CB after modified 1.0%, the carboxyl group content on modified CB is evaluated as 27.9% from (33.8%−1.0%)−(7.0%−2.1%) based on the above data. Using the same procedure as total weight loss deducting that below 200 °C, the content of PAA coated on the surface of MNPs is 26.8% and the total proportion of organic species for CB-MNP-3.0 is given as 20.0%. Lower organic content of CB-MNP-3.0 than modified CB and MNPs indicate that less PAA are coated on the surface of MNPs. This can be attributed to steric hindrance resulting from the MNPs loaded on the surface of modified CB.

Cubic magnetite is ferromagnetism while nanometer scale particles with the size below 30 nm exhibits superparamagnetism. Vibrating sample magnetometer (VSM) was used for determination of magnetic...
properties of the CB-MNP nanocomposites. The average size of MNPs determined by TEM and XRD is below 10 nm. As expected, no remanence and coercivity is shown for MNPs and CB-MNP-3.0, indicating that the nanoparticles are superparamagnetic at room temperature (figure 7). The saturated mass magnetization of MNPs and CB-MNP-2.0 were estimated as 73.7 and 70.2 emu g$^{-1}$, respectively, after the non-magnetic contents was deducted according to total weight loss of TGA results (figure 6). High magnetization allows for CB-MNP-3.0 with rapid magnetic response as shown in figure. Lower saturated mass magnetization of CB-MNP-3.0 than MNPs may result from calculating error by TGA data or a little bit size difference between them.

3.3. Water stability of CB-MNP composites
High water stability and fast magnetic response are very important for fast removal of heavy ions by absorption. We measured the hydrodynamic size distribution of CB-MNP-2.0 at different time as shown in figure 8(a). The size distribution still shows single peak (figure 8(a)) and the average size has no obvious change after 24 h (figure 8(b)), indicating that CB-MNP are very stable at natural state. Water stability of four CB-MNP samples was compared in figure S2. CB-MNP-0.5 starts to produce precipitate within 30 s and deposits completely after 30 min CB-MNP-1.0 begins to produce precipitate with 30 min but do not deposits completely after 24 h. CB-MNP-2.0 and CB-MNP-3.0 are very stable and no visible deposits were observed after 24 h. The results indicate that larger proportion of added CB leads to higher water stability. Lower proportion of CB means that each CB

![Figure 6. TGA curves of CB before modified, CB after modified, MNPs and CB-MNP-2.0.](image1)

![Figure 7. Magnetization curves of MNPs(1) and CB-MNP-2.0(2) at room temperature.](image2)
will be loaded with more MNPs, which results in larger hydrodynamic size (figure 5(c)) and lower water stability. Figure S4 shows the stability of CB-MNP-2.0 at different pH values. It is similar to CB-N12-T100 that CB-MNP-2.0 at pH $= 5$ deposits completely after 30 min and at pH $= 7$ and 8 are very stable even after 24 h. Low stability is attributed to low charges on the surface at pH value close to isoelectric point (pH $= 4$) of carboxyl groups. Interestingly, CB-MNP-2.0 is stable under natural state but it can be magnetically attracted and concentrated within 5 min under 0.2 T of applied field. These results reveal that the CB-MNP-2.0 composite owns high water stability as well as fast magnetic response, which facilitates to fast absorption removal of heavy ions.

3.4. Absorption removal of cadmium ions
The kinetic curves and removal rates of Cd$^{2+}$ adsorption by CB-MNP-2.0 are shown in figure 9. It can be seen that the adsorption rate of Cd$^{2+}$ is very fast before absorption equilibrium. The adsorption is almost close to equilibrium within 10 min. The removal rate decreases with the increasing the initial concentration of Cd$^{2+}$ solution. The removal efficiency and absorption capacity are 71.41% and 39.99 mg·g$^{-1}$ for the initial concentration of $5.6 \times 10^{-5}$ mol·l$^{-1}$ (5.6 mg·l$^{-1}$) and 38.10% and 42.67 mg·g$^{-1}$ for the initial concentration of $1 \times 10^{-4}$ mol·l$^{-1}$ (11.2 mg·l$^{-1}$). The removal efficiency dropped considerably while the absorption capacity is a little higher with the rising of the initial concentration of Cd$^{2+}$ solution, indicating that the absorption capacity is close to up limit at the initial concentration of $5.6 \times 10^{-5}$ mol·l$^{-1}$. Removal efficiency and equilibrium time for PAA modified graphene composite, PAA/GO/Fe$_3$O$_4$, are 85% and 30 min under the initial Cd$^{2+}$ concentration 10 mg·l$^{-1}$ and the amount of absorbents 1.5 mg, respectively [22]. Herein, removal efficiency 38.10% at 11.2 mg·l$^{-1}$ of initial concentration of Cd$^{2+}$ is much smaller than that of PAA/GO/Fe$_3$O$_4$, which may account for lower absorption amount, a avlue of 0.4 mg calculated as (2 mg·ml$^{-1}$·200 μl). Also, CB-MNP has a shorter equilibrium time than that of PAA/GO/Fe$_3$O$_4$. Thus, CB-MNP has comparable absorption performance to PAA/GO/Fe$_3$O$_4$.

To probe into the absorption kinetics, the pseudo-first-order, pseudo-second-order kinetic and Elovich models were used for fitting the absorption behavior of Cd$^{2+}$ as follows:
Adsorption. This could be explained by the reason that the adsorption of Cd$^{2+}$ and 31.27 mg l$^{-1}$ becomes more significant when the concentration increases from 5.6 mg l$^{-1}$ to 11.2 mg l$^{-1}$. The kinetic data of Cd$^{2+}$ adsorption at different concentrations was fitted with the pseudo-first-order and pseudo-second-order kinetic models as shown in figure 10 and table 1. For the Cd$^{2+}$ solutions with initial concentrations of 5.6 mg l$^{-1}$ and 11.2 mg l$^{-1}$, the equilibrium adsorption capacities are 31.06 mg g$^{-1}$ and 31.27 mg g$^{-1}$, respectively. The experimental results for absorption capacities are 39.99 mg g$^{-1}$ and 42.67 mg g$^{-1}$, which fits better with the pseudo-second-order kinetic models, revealing that the adsorption process is dominated by chemical adsorption.

The effect of pH on Cd$^{2+}$ removal efficiency is investigated as shown in figure 11(a). The removal efficiency rises gradually with the increase of pH values in the range of pH 5 to 10, which can be attributed to the formation of Cd(OH)$_2$ deposits under alkaline condition, promoting the removal of Cd$^{2+}$.

Actually, there are interfering ions such as PO$_4^{3-}$, Cl$^-$, SO$_4^{2-}$ and CO$_3^{2-}$ co-existing with Cd$^{2+}$ in waste or natural water. Herein, the effect of anion ions with different strengths on the removal efficiency of Cd$^{2+}$ was evaluated. As displayed in figure 11(b), the removal efficiency of Cd$^{2+}$ remains unchanged when the concentration of four interfering anion ions, PO$_4^{3-}$, Cl$^-$, SO$_4^{2-}$ and CO$_3^{2-}$, is as low as 1 mM. However, the removal efficiency of Cd$^{2+}$ is enhanced when the concentration of PO$_4^{3-}$ and CO$_3^{2-}$ reaches to 10 mM, especially promoted by the addition of PO$_4^{3-}$ for Cd$^{2+}$ adsorption. This could be explained by the reason that the adsorption of Cd$^{2+}$ by CB-MNP-2.0 mainly included chemical adsorption and electrostatic adsorption, which could be enhanced by the anion coexistence.

In summary, the prepared composite material CB-MNP-2.0 exhibited excellent performance for removal of Cd$^{2+}$. At the initial pH = 7, the adsorption capacity of CB-MNP-2.0 is 39.99 mg g$^{-1}$, matching with absorptive kinetics of pseudo-second-order models. The increase of pH value can promote the removal of Cd$^{2+}$. The highest removal rate of Cd$^{2+}$ reaches to 81.33% at pH = 10 and an initial concentration 5.6 mg l$^{-1}$. Removal rate of Cd$^{2+}$ can also be enhanced by coexisting anions.

Table 1. The parameters of pseudo-first/second-order fitting of Cd$^{2+}$ over CB-MNP-2.0.

| Cd$^{2+}$ (mg l$^{-1}$) | q_e exp. (mg g$^{-1}$) | $K_1$ (min$^{-1}$) | $R^2$ | q_e cal. (mg g$^{-1}$) | $K_2$ (g/(mg min$^{-1}$)) | $R^2$ | q_e cal. (mg g$^{-1}$) |
|------------------------|-----------------|-----------------|-------|-----------------|-----------------|-------|-----------------|
| 5.6                    | 39.99           | 0.1467          | 0.6219| 31.06           | 0.0253          | 0.9987| 39.24           |
| 11.2                   | 42.67           | 0.1493          | 0.6624| 31.27           | 0.0235          | 0.9999| 42.44           |

Pseudo-first-order kinetic model

$$\ln (q_e - q_t) = \ln q_e - k_1t$$

Pseudo-second-order kinetic model

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$

Where $q_e$ (mg g$^{-1}$) is the equilibrium adsorption capacity; $q_t$ (mg g$^{-1}$) is the adsorption capacity at the given time $t$; $k_1$ (l/min) is the rate constant for the quasi-first-order kinetic equation; $k_2$ (g/(mg min$^{-1}$)) is the rate constant for the pseudo-second-order equation. The other parameters are different constants of kinetic models.

The kinetic data of Cd$^{2+}$ adsorption at different concentrations was fitted with the pseudo-first-order and pseudo-second-order kinetic models as shown in figure 10 and table 1. For the Cd$^{2+}$ solutions with initial concentrations of 5.6 mg l$^{-1}$ and 11.2 mg l$^{-1}$, the equilibrium adsorption capacities are 31.06 mg g$^{-1}$ and 31.27 mg g$^{-1}$, fitting with the pseudo-first-order kinetic models ($R^2 = 0.9987$) (figures 10(a)) and 39.99 mg g$^{-1}$ and 42.44 mg g$^{-1}$ with the pseudo-second-order kinetic models ($R^2 = 0.9999$) (figure 10(b)), respectively. The experimental results for absorption capacities are 39.99 mg g$^{-1}$ and 42.67 mg g$^{-1}$, which fits better with the pseudo-second-order kinetic models, revealing that the adsorption process is dominated by chemical adsorption.
4. Conclusion

CB-MNP nanocomposites, modified carbon black loaded with superparamagnetic MNPs, were successfully fabricated by cheap commercial carbon black as a substitute for expensive carbon nanotube or graphene to fabricate. Modified CBs with a large number of carboxyl groups on the surface and owning high water stability were firstly prepared by original commercial CB partial oxidized in the presence of nitric acid. The size of modified CB can be tuned by different temperature and the CB dispersion remains stable and have no obvious precipitate observed even after for 48 h. Subsequently, four CB-MNP samples were facilely prepared by iron precursors (the ratio of ferrous to ferric is 1:2) added into the above CB dispersion and tuned pH = 10, finally added polyacrylic acid solution under sonication. The crystal phase of MNPs was determined by high resolution TEM, SAED, XRD and raman spectra. Results from TEM and XRD show that the average particle size of MNPs for all of four CB-MNP samples is about 7.5 nm. Water stability and magnetic response can be controlled by changing the proportion of CB and iron precursor. CB-MNP-2.0 is stable under natural state but it can be magnetically attracted and concentrated within 5 min under 0.2 T of applied field, revealing that the CB-MNP-2.0 composite owns high water stability as well as fast magnetic response, which facilitates to fast absorption removal of heavy ions. As a proof-of-concept, CB-MNP-2.0 was used for absorption removal of cadmium ions. Excellent performance was demonstrated with the removal efficiency of 71.41% and removal capacity of 39.99 mg·g⁻¹ at the initial concentration of Cd²⁺ as 5 × 10⁻⁵ mol·l⁻¹. The effects of initial concentration of Cd²⁺, pH value and interfering anion ions were also investigated and the results indicate the potential application of CB-MNP in fast removal of heavy metal ions.

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